Synthetic and structural studies on early transition metal siloxides

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by

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Abstract

ABSTRACT

Synthetic and Structural Studies on Early Transition Metal Siloxides

n-Bu_3SiOH was prepared from both *n*-Bu_3SiH and *n*-Bu_3SiCl. Reactions of *n*-Bu_3SiOH with NaH, $LiBu^n$, MCl_5 (M = Ta or Mo) and Cp_2MCl_2 (Cp = η^5-C_5H_5, M = Ti or Zr) were investigated, in some cases using the base Et_3N as a hydrogen chloride acceptor. $Na^+(OSiPh_3)^-$ was prepared from the reaction of Ph_3SiOH with NaH, but in poor yield. Ph_3SiOH was reacted with $TaCl_5$, but the product, if formed at all, was intractable. When Ph_3SiOH was reacted with Cp_2MCl_2 (M = Ti or Zr) products were isolated and characterised, *viz.* $[Cp_2TiCl(OSiPh_3)]_n$ (n = 1 or 2) and $Cp_2Zr(OSiPh_3)_2$. Single crystals $Cp_2Zr(OSiPh_3)_2$ were studied using X-ray photographic techniques. They crystallise in the monoclinic system with a = 35.7, b = 10.4, c = 21.1 Å, β = 97.7 °, V = 7763 Å^3. A full crystal structure analysis was not possible due to failure of the diffractometer software to locate the monoclinic unit cell determined by photographic methods. Ph_3SiOH was also reacted with $Cp^*_2ZrCl_2$ (Cp^* = η^5-C_5Me_5) and the product was tentatively assigned to be $Cp^*_2Zr(OSiPh_3)_2$ as a pure sample could not be obtained. An interesting spiro-compound, $\overline{Ti[OSiPh_2(OSiPh_2)_3O]}_2$, was prepared from $Ph_2Si(OH)_2$ and Ti(*n*-BuO)$_4$ and the crystal structure determined by X-ray crystallography. It crystallises in the monoclinic system, space group $P2_1/n$, a = 13.805(5), b = 27.545(5), c = 23.476(9) Å, β = 94.41(3) °, V = 8901(5) Å^3, Z = 4, R = 0.0831 for 5528 reflections with $I_{rel} > 2\sigma(I_{rel})$.

Abbreviations used in Text

ABBREVIATIONS USED IN TEXT

Me	=	methyl group, $-CH_3$
Ph	=	phenyl group, $-C_6H_5$
Bu	=	butyl group, $-C_4H_9$
NMR	=	nuclear magnetic resonance (m = multiplet, s = singlet, br. s = broad singlet d = doublet, t = triplet, q = quartet)
Cp	=	cyclopentadienyl group, C_5H_5
DME	=	dimethoxyethane
py	=	pyridine
tritox	=	tri-*t*-butylmethoxyl group, $-OC[C(CH_3)_3]_3$
silox	=	tri-*t*-butylsiloxyl, $-OSi[C(CH_3)_3]_3$
THF	=	tetrahydrofuran
ppm	=	parts per million
TLC	=	thin-layer chromatography
dec.	=	decomposition
sublim.	=	sublimation
m.p.	=	melting point
DMSO	=	dimethylsulfoxide
XRF	=	X-ray fluorescence
Cp^*	=	1,2,3,4,5-pentamethylcyclopentadienyl group, $C_5(CH_3)_5$
VSEPR	=	valence shell electon pair repulsion
TMS	=	tetramethylsilane
b.p.	=	boiling point
δ_H	=	proton NMR
m/z	=	mass-to-charge ratio
D	=	density

Table of Contents

TABLE OF CONTENTS

Chapter One

Introduction

CHAPTER 1
INTRODUCTION

Introduction to organosilicon chemistry

The synthesis of organosilicon compounds was first documented in 1865 by Friedel and Crafts,[1] who reported the synthesis of tetraethylsilane from diethyl zinc and silicon tetrachloride. Kipping and co-workers[2] at the University of Nottingham were the first to carry out systematic studies on organosilanes, between 1898 and 1939†. Interest in organosilicon chemistry increased dramatically in the 1940s following the success of silicone polymers. Presently, organosilanes are found in applications such as solutions to synthetic problems, healthcare products and computer chips on the industrial and commercial fronts. Organosilanes are being studied theoretically, investigated as synthetic reagents and pushed even further in the quest for important and useful applications.[3]

At this stage it seems pertinent to describe the nomenclature of organosilanes. A description of the basic nomenclature can be found below.

Basic nomenclature of organosilanes [3]

- Named as derivatives of silane or disilane, *etc.*:

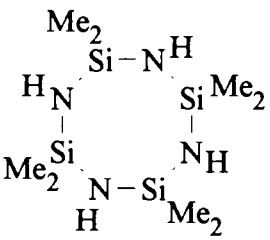
SiH_4	=	silane
H_3SiSiH_3	=	disilane

† This contribution was recognised by the American Chemical Society which presents the Frederick Stanley Kipping award biannually for "distinguished achievement in research in organosilicon chemistry".

- When different groups are attached to the silicon, the groups are named in alphabetical order:

Me_2SiCl_2	=	dichlorodimethylsilane
$MePhSiH_2$	=	methylphenylsilane

- Silazanes are named as disilazane, trisilazane and so forth depending on the number of silicon atoms in the structure:

$H_3SiNHSiH_2NHSiH_3$	=	trisilazane
	=	1,1,3,3,5,5,7,7-octamethylcyclo-tetrasilazane

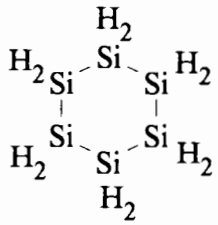
- Siloxanes are named similarly:

$H_3SiOSiH_3$	=	disiloxane
$Ph_3SiOSiPh_3$	=	hexaphenyldisiloxane
$Me_3SiOSiMe_2OSiMe_2CH{=}CH_2$	=	1-vinylheptamethyltrisiloxane

- General names when the silicon group must be named as a unit:

H_3Si-	=	silyl
$H_2Si{=}$	=	silylene
H_3SiO-	=	siloxanyl
n-Bu_3Si-	=	tri-*n*-butylsilyl
t-$BuMe_2Si$-	=	*t*-butyldimethylsilyl
t-Bu_3SiO-	=	tri-*t*-butylsiloxy

- Cyclic silanes:



= cyclohexasilane

- Hydroxy derivatives are named as silanols

H_3SiOH	=	silanol
$Ph_2Si(OH)_2$	=	diphenylsilanediol
t-$BuSi(OH)_3$	=	*t*-butylsilanetriol
Ph_3SiONa	=	sodium triphenylsilanoate

- Organic nomenclature is favoured over organosilicon nomenclature

$Me_3SiCH(OH)CH_3$	=	1-trimethylsilylethanol
$PhCO_2SiEt_3$	=	triethylbenzoate.

Twenty-five percent of the earth's crust is composed of silicon, in the form of polysilicates, compared to carbon comprising only one percent. Silicon occurs in three isotopes, namely ^{28}Si (92.2 %), ^{29}Si (4.2 %) and ^{30}Si (3.1 %) with nuclear spins I = 0, ½ and 0 respectively. ^{29}Si NMR is thus possible and has added much to the knowledge of silicon-containing species.

Synthesis of organosilanes

Organosilanes do not occur naturally, but have their origins in silicon dioxide.

In 1924 Berzelius found that silicon dioxide could be converted to silicon metal *via* the fluoride (see Eqns 1 and 2).

$$SiO_2 + 4\ HF \longrightarrow SiF_4 + 2\ H_2O$$

(Equation 1)

$$SiF_4 + 2\ KF \longrightarrow K_2SiF_6 \xrightarrow{4\ K} 6\ KF + Si$$

(Equation 2)

A more commonly used preparation of silicon metal involves reacting silicon dioxide with carbon and then converting it to the oxidising forms (see Eqns 3–5).

$$SiO_2 + 2\ C \xrightarrow{\text{electric furnace}} Si + 2\ CO$$

(Equation 3)

$$Si + 2\ Cl_2 \longrightarrow SiCl_4$$

(Equation 4)

$$Si \xrightarrow{HCl} HSiCl_3$$

(Equation 5)

The synthesis of organohalosilanes by a direct process, known as the Rochow reaction, was independently discovered by E. Rochow and R. Muller.[4-6] Organic halides are reacted directly with silicon metal in the presence of an electron-transfer catalyst, usually copper (see Eqn 6).

$$RX + Si \xrightarrow{\Delta\ /\ Cu} RSiX_3 + R_2SiX_2 + R_3SiX + R_3Si + \text{others}$$

(Equation 6)

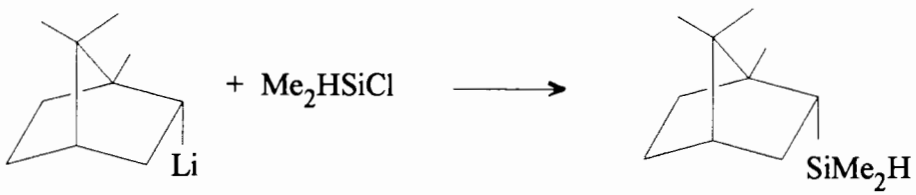
Dichlorodimethylsilane is an important precursor to the polydimethylsiloxanes so the reaction conditions are controlled to maximise its yield. Methyltrichlorosilane and trimethylchlorosilane are 'by-products' of the process and are useful for the preparation of other organosilanes.

With the use of different electron-transfer catalysts, the preparation of vinyl- and arylsilanes is also possible.

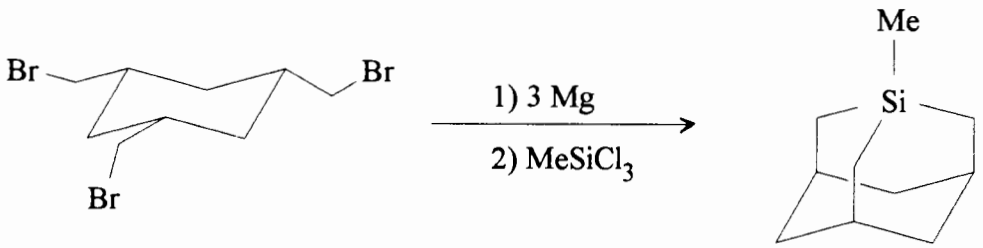
Examples of the preparation of some organosilanes can be seen in Equations 7–13.[3]

$$Me_2SiCl_2 \xrightarrow{PhMgBr} Me_2PhSiCl \xrightarrow{CH_2=CHMgBr} Me_2PhSiCH=CH_2$$

(Equation 7)



(Equation 8)



(Equation 9)

$$PhSiH_3 + PhMgBr \longrightarrow Ph_2SiH_2$$

(Equation 10)

$R_3SiH + In\cdot \longrightarrow R_3Si\cdot + In-H$ In = radical initiator

(Equation 11)

$R_3Si\cdot + R'CH=CH_2 \longrightarrow R'\dot{C}H-CH_2SiR_3$

(Equation 12)

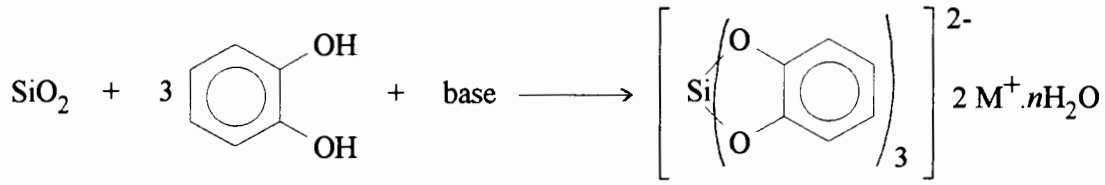
$R'\dot{C}H-CH_2SiR_3 + R_3SiH \longrightarrow R'CH_2CH_2SiR_3 + R_3Si\cdot$

(Equation 13)

The organosilane products accessible by reaction of silanes with organometallic reagents (Eqns 7–10) are only limited by the ability to prepare the appropriate organometallic reagent.[7]

The reaction sequence illustrated by equations 11 to 13 describes the addition of a silicon-hydrogen bond to a carbon-carbon bond *via* a free radical pathway (initiated by heat, peroxides or irradiation). This type of reaction is known as hydrosilylation.[8,9]

A challenging problem for chemists is to find a direct way of transforming silica (SiO_2) into organosilanes without prior conversion to metallic silicon. Attempts have been reported, but appear not to have been very successful.[10-13] Boudin *et al.*,[14] however, described a possible route for the formation of organosilanes from silica using hypervalent silicon species. They employed a hexaco-ordinated anionic species of silicon, which originated from the work of Rosenheim *et al.*[15] (see Eqn 14). These anionic species were subjected to nucleophilic attack of organometallic reagents (RLi, RMgX) leading to the formation of silicon-carbon bonds (see Eqn 15).

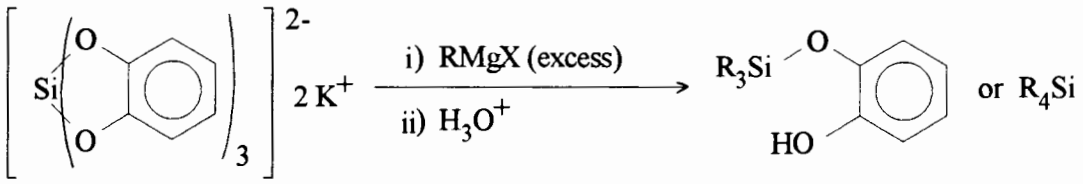


base = NH_4OH, KOH, *etc.*

M^+ = NH_4^+, ($n = 9$)

M^+ = K^+, ($n = 8$)

(Equation 14)



(Equation 15)

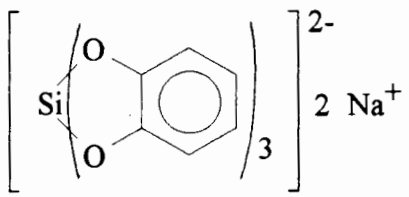
Of specific interest to our study are the silanols: tri-*t*-butylsilanol (*t*-Bu_3SiOH), tri-*n*-butylsilanol (*n*-Bu_3SiOH), triphenylsilanol (Ph_3SiOH) and diphenylsilanediol [$Ph_2Si(OH)_2$].

Several preparative methods of the first trialkylsilanol, *viz.* triethylsilanol, were reported in 1872 by Ladenburg.[16,17] Some of these methods involved the addition of cold, dilute ammonium hydroxide to triethylchlorosilane and the heating of triethylsilyl acetate with sodium carbonate. Ladenberg also observed the formation of hexaethyldisiloxane when the silanol was exposed to phosphorus pentoxide or sulfuric acid. Sodium was observed to react readily with the silanol to give sodium triethylsilanoate on warming or addition of dry ether. Other, earlier, reports of preparation of silanols and sodium silanoates can be found in refs 18-21.

The preparation of tri-*t*-butylsilane (*t*-Bu_3SiH) was first reported by Dexheimer and Spialter[22] in 1975 and involved reacting di-*t*-butyldifluorosilane (*t*-Bu_2SiF_2) with

t-butyllithium in refluxing cyclohexane. The silanol derivative, *t*-Bu_3SiOH was then formed by reaction of *t*-Bu_3SiH with potassium hydroxide in a mixture of ethanol, water and THF. Subsequently, Weidenbruch *et al.*[23] also reported the preparation of the silane and the silanol: the silane was prepared by treatment of *t*-BuLi with $HSiCl_3$ or $HSiF_3$; as above, the silanol was prepared using KOH.

As described earlier, Boudin *et al.*[14] reported the preparation of numerous silanes. The synthesis of *n*-Bu_3SiOH was included in their work and involved reacting a dianionic hexaco-ordinated silicon complex with the Grignard reagent, *n*-BuMgCl, followed by acid hydrolysis (see Eqn 16).



i) *n*-BuMgCl (excess)
ii) H_3O^+

n-Bu_3SiOH

(Equation 16)

Other preparations of *n*-Bu_3SiOH from *n*-Bu_3SiH have been reported by Spialter *et al.*[24] and Duffaut *et al.*.[25] The former group described an interesting preparation of the silanol by reacting the silane with ozone. The conversion is rapid and quantitative, unlike the analogous oxidation of hydrocarbons which is much slower and produces a variety of products.[26,27] Duffaut *et al.*[25] prepared *n*-Bu_3SiOH by reacting $AgNO_3$ with the silane. Both research groups also documented the preparation of Ph_3SiOH by similar methods to those used for the preparation of *n*-Bu_3SiOH.

The preparation of disiloxanes is also well-documented in the literature. Glidewell and Liles[28] reported the preparation and determination of the crystal and molecular structure of hexaphenyldisiloxane, $O(SiPh_3)_2$, where Ph_3SiOH and an excess of KOH

were reacted together, after which chlorophenylsilane was added. Suwinska *et al.*[29] described the crystal and molecular structures of two similar compounds involving hexaphenyldisiloxane as the clathrate with benzene and piperidine as guest molecules [*i.e.* $(Ph_3Si)_2O.½C_6H_5$ and $(Ph_3Si)_2O.2C_5H_{11}N$]. Wiberg *et al.*[30] detailed the synthesis, molecular and crystal structure of hexa-*t*-butyldisiloxane, $(t\text{-}Bu_3Si)_2O$, which was prepared from bis(silyl)triazene, $t\text{-}Bu_3SiN{=}N\text{-}NHSi(t\text{-}Bu)_3$, water and triethylamine. Hossian and Hursthouse[31] documented the crystal structure of 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $[Ph_2Si(OH)]_2$, as prepared by Prescott and Selin.[32]

From the pioneering work by Ladenburg and Friedel[16,33] in the 1870s until the middle of the twentieth century, there was considerable interest in the alkali metal salts of silanols. Mono-organo- and diorgano-salts were prepared by the action of alkali on siloxanes and silanols.[33] Triorgano-salts were prepared from the action of sodium metal on the silanol. Of particular interest to the preparation of transition metal siloxides is the preparation of sodium triphenylsilanoate, documented by Schlenk *et al.*[34] and Tatlock and Rochow.[35]

Early transition metal siloxides

Complexes consisting of early transition metals and various siloxyl ligands have been extensively reported in the literature. A list of selected metal siloxides (1–26) can be seen in Table 1. It should be emphasised that this list is not to be regarded as comprehensive because it represents only a selection of the published work in this field but it does serve to illustrate typical coordination numbers of the metals and commonly employed ligands with early transition metals.

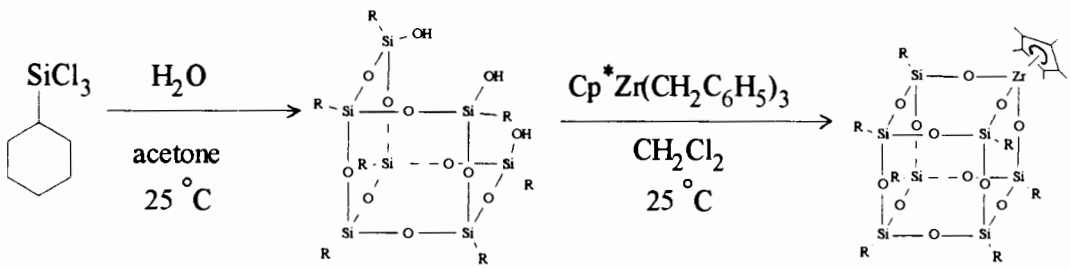
Table 1 - A selection of early transition-metal siloxides.

1	$Ti(OSiMe_3)_2(OPr^i)_2$ [36]	2	$Ti(OSiPh_2Me)_4$ [36]
3	$Ti(O_2SiPh_2)_2$ [37]	4	$Ti(OSiPh_3)_4$ [38]
5	$Cp_2Ti(OSiPh_3)_2$ [39]	6	$\overline{Ti(OSiPh_2OSiPh_2O)}_2$ [40]
7	$\overline{Ti[OSiPh_2(OSiPh_2)_3O]}_2$ [41†]	8	*cis*-$\{\overline{Ti[OSiPh_2(OSiPh_2)_2O]}_2(py)_2\}$ [40†]
9	$Cp_2Zr(OSiPh_3)_2$ [42]	10	$Zr(OSiPh_3)_4$ [43]
11	$[Zr(OSiMe_3)_4]_2$ [43]	12	$(DME)ZrCl_2(OSiPh_3)_2$ [42†]
13	$Li_2[\overline{Zr(OSiPh_2OSiPh_2O)_3}]$-.3py [40†]	14	$(NEt_2H_2)_2[\overline{Zr(OSiPh_2OSiPh_2O)_3}]$ [40]
15	$(NEt_2H_2)_2$-$[\overline{Hf(OSiPh_2OSiPh_2O)_3}]$ [40]	16	$Hf(OSiPh_3)_4$ [43]
17	$V(OSiPh_3)_4$ [43]	18	$VO(OSiPhEt_2)_3$ [43]
19	$VOCl_2(OSiMe_3)$ [43]	20	$Nb(OSiMe_3)_5$ [44]
21	$Nb(OSiMeEt_2)_5$ [44]	22	$Ta(OSiMe_3)_4$ [44]
23	$Ta(OSiMe_2Pr^i)_5$ [44]	24	$Ta[OSi(C_6H_4Me\text{-}2)_3]Me_3Cl$ [45†]
25	$(Bu^t_3SiO)MoO_3^-$ [46†]	26	$(Ph_3SiO)MoO_3^-$ [46†]

† crystal structure published

Polyhedral oligometallasilsesquioxanes (POMSS)

An interesting class of organosilicon transition metal compounds are the polyhedral oligometallasilsesquioxanes (POMSS). They have been extensively studied by Feher and co-workers[47-50] in an attempt to develop a suitable model system which can be used to simplify the study of silica surface complexes. Heterogeneous silica-supported transition metal compounds play an increasingly important role as catalysts in the petrochemical industry and this has stimulated intense interest in the chemical processes which occur on the surfaces of such heterogeneous catalysts. Detailed mechanistic studies are inherently difficult due to the complicated atomic structure of the silica surface: hence the potential usefulness of the POMSS molecules which offer a simplied model of this surface. The POMSS molecules, analogous to the silicon-oxygen frameworks of polyhedral oligosilsesquioxanes (POSS), were designed to mimic surface sites and possess three hydroxyl groups interacting with a single transition metal atom. A typical example of the preparation of a POMSS can be seen below in Eqn 17.



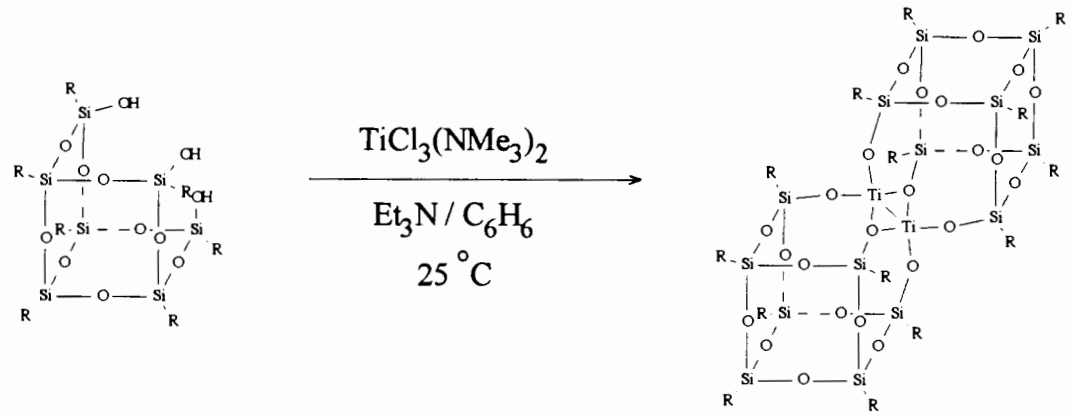
27 28

($R = c\text{-}C_6H_{11}$)

(Equation 17)

Spectroscopic and structural studies of these compounds have been performed and are reported in detail by Feher.[47]

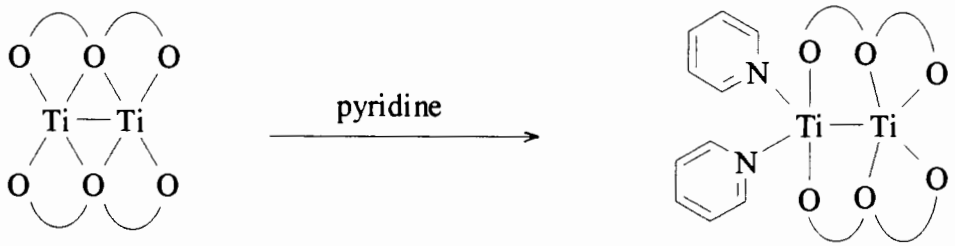
In a later publication by Feher *et al.*,[48] efforts to synthesise Ti(III) complexes (*i.e.* a bare titanium atom situated on the vertex of the polyhedron) from the trisilanol, 27, were reported. This was not achieved, but a siloxy-bridged dinuclear complex was obtained (see Eqn 18).



27 29

(Equation 18)

Additional ligands were co-ordinated to one of the titanium atoms when 29 was reacted with pyridine (see Eqn 19).



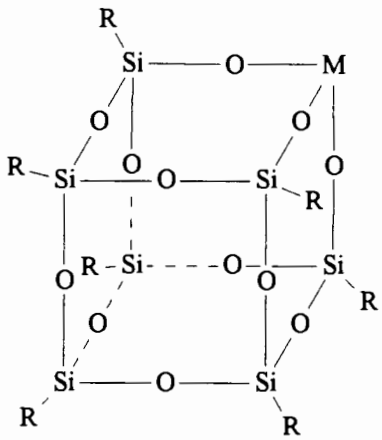
29 30

(Equation 19)

X-Ray crystal structures were reported of both 29 and 30.[47]

The mechanism of formation of such dimeric complexes as 29, was not known, but was greatly favoured over that of pyramidalised monomers (of which 28 is an example) for the trisilanol ligand, 27, used. It was proposed that the use of smaller transition metal ions, such as V(III), Cr(III) or Fe(III), would favour the formation of the pyramidalised monomers.

Other so-called corner-capping reactions involving the trisilanol, 27, have been reported by Feher *et al.*[49] Using $MeGeCl_3$, $MeSnCl_3$ and $R'SiCl_3$, products 31a–d were successfully prepared (see below).



31a M = GeMe

31b M = SnMe

31c M = SiR' R' = *p*-$C_6H_4CH_2Cl$

31d R' = *p*-$C_6H_4CCl_3$

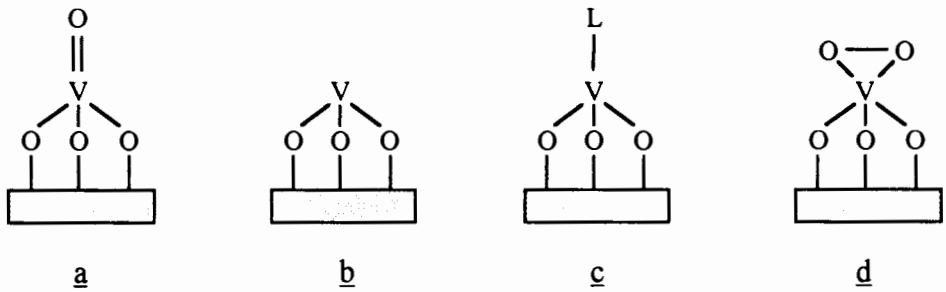
Species 31c and 31d represent mixed octameric silsesquioxane with seven chemically inert cyclohexyl rings and one reactive functional group (R').

Although trisilanol, 27, represents one of the best models of silica developed to date, it is limited to modelling surface sites possessing three hydroxyl groups. This limitation was recognised by Feher *et al.* and syntheses of several silsesquioxanes

derived from 27 that may also be useful as models for silica, have been developed *via* trimethylsilylation or dehydration.[49]

More recently, Feher *et al.*[50] have extensively investigated vanadium-containing silsesquioxanes as silica-supported vanadium complexes that can be useful catalysts for a variety of important transformations such as the oxidation of methane and other hydrocarbons and the polymerisation of α-olefins.

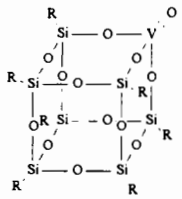
Trisilanol, 27, provides an excellent structural model for the silica-supported vanadium catalysts as a number of studies[50] have implicated 'three-legged' surface complexes as important surface species (see Figure 1).



a b c d

Figure 1 - "Three-legged" surface complexes of silica-supported vanadium complexes.

Complexes to model a–c (Figure 1), 32–36b are reported (see overleaf), although 33 and 34 were only observed in solution and were not isolated.[50]



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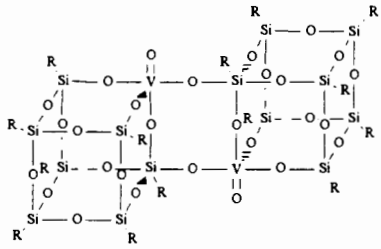

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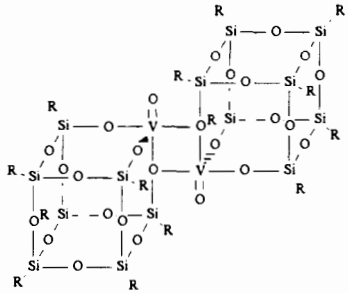
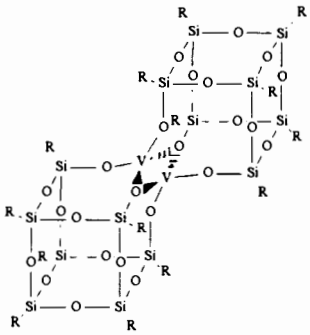
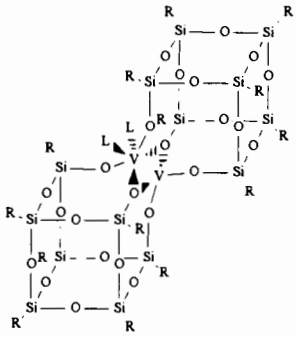


34



35



36a L = pyridine

36b MeCN

As is apparent from the products synthesised, a limitation of this class of silica models is that highly reactive, low co-ordination number transition metal complexes have a tendency to oligomerise. Trisilanol, 27, is neither bulky nor rigid enough to prevent the formation of siloxy-bridged dimers. The flexibility of the silsesquioxane framework, which is an advantage in developing a versatile model applicable to any metal ion, will necessarily allow the contortions by which a highly reactive metal complex will find alternative structures that reduce co-ordination unsaturation.

This is not a serious limitation, as incompletely condensed silsesquioxanes still provide excellent models for hydroxylated silica surface sites.

Tri-t-butylsiloxane compounds of transition-metals

This area of organometallic silane chemistry has been well documented by Wolczanski and co-workers.[51-57] Initially their work focused on tri-*t*-butylmethoxide.[58,59] The tri-*t*-butylmethoxy ligand, $t\text{-}Bu_3CO^-$, will be referred to as tritox.

An interesting challenge facing the organometallic chemist is the generation of organo transition metal complexes possessing the degree of co-ordinative unsaturation necessary for observation of metal-centered reactivity.[60] LaPointe *et al.*[51] proposed that a sterically saturated metal centre, which can remain electronically deficient, could be a plausible solution. This prompted their preparation of tritox-metal complexes involving the direct treatment of group 4 halides with (tritox)H. A list of these complexes (37–47) can be found in Table 2 below.

Table 2 - A list of tritox-containing transition-metal complexes prepared by Wolczanski and co-workers.[51,58]

37	$(tritox)_2ZrCl_3.Li(OEt_2)$ †	38	$(tritox)_2ZrCl_2$	
39	$(tritox)_2TiCl$ ‡	40	$(tritox)_2TiCl_2$	
41	$(tritox)TiCl_3$	42a	$(tritox)_2M(CH_3)_2$	M = Zr
		42b		M = Ti
43	$(tritox)Ti(CH_3)_3$	44	$(tritox)Zr(CH_2Ph)_3$	
45	$(tritox)Zr[CH_2C(CH_3)_3]_3$	46	$(tritox)_3ZrCH_3$	
47	$(tritox)Nb_2TaCl_2$			

† - crystallographic structure published

‡ - tentative formulation.

It was found to be impossible to extend the preparative study to group 5 because of the facile heterolytic degradation of the C–O bond in the (tritox)M species. Tri-*t*-butylsiloxide was thought to be an attractive alternative to tritox because of the strength of silicon-oxygen bonds and their kinetic stability with respect to heterolytic Si–O cleavage.[51] The tri-*t*-butylsiloxyl ligand, *t*-Bu_3SiO^-, will be referred to as silox. Weidenbruch *et al.*[61] pioneered the study of silox compounds of transition metals with the preparation of complexes 48 to 52 (see Table 3 below).

Table 3 - Silox-containing transition metal complexes prepared by Weidenbruch *et al.*.[61]

48	$[(silox)_2VO]_2O$	49	$(silox)_2VO(OCH_3)$	
50	$(silox)_3NbCl_2$	51a	$(silox)MO_2$	M = Cr
		51b		M = Mo
52	$(silox)_3SiOReO_3$			

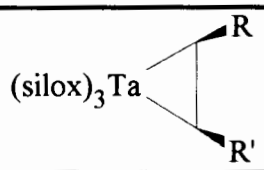
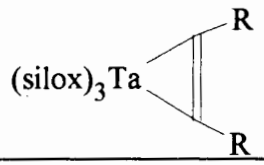
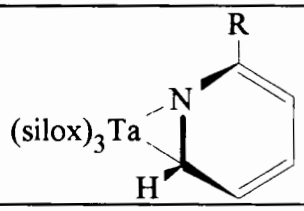
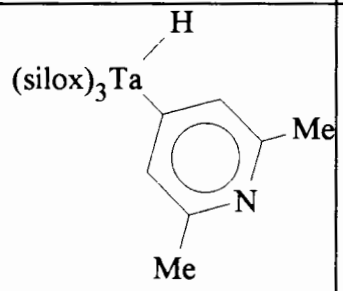
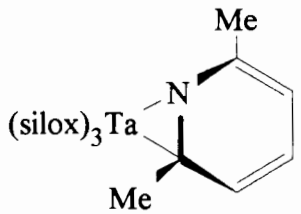
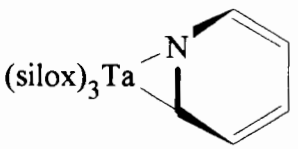
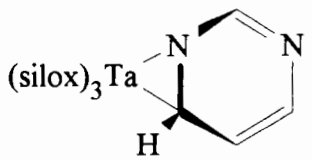
This preparative study was extended by LaPointe *et al.*[51] who chose to use the silox ligand in the form of Na(silox). Numerous silox-containing transition metal complexes have been reported by Wolczanski and co-workers (53–95), a list of which can be found in Table 4 overleaf.

Table 4 - Silox-containing transition-metal complexes prepared by Wolczanski and co-workers; 53–61,[51] 62–68,[52] 69–72,[53] 73–74,[54] 75–80,[55] 81[56] and 82–94.[57]

53	$(silox)_2TaCl_3$	54	$(silox)_2TaMe_3$
55a	$(silox)_2TaR_3$ R =Me	56	$(silox)_2Ta{=}CHPh(CH_2Ph)$
55b	R =CH_2Ph	57	$(silox)_2TaCl_2(CH_2Ph)$
58	$(silox)TaNp_3Cl$	59	$(silox)_2TaNp_2Cl$
60	$(silox)_2NbTa{=}C(H)CMe_3$	61	$(silox)Nb_2Ta{=}C(H)CMe_3)$
62	$(silox)_3Ta$	63	$(silox)_3Ta{=}O$
64	$[(silox)_3Ta]_2(\mu\text{-}C_2)$ §	65	$(silox)_2(H)TaOSiBu^t{}_2CMe_2CH_2$
66a	$(silox)_3Ta(\eta^2\text{-}C_2H_3R)$ R = H	67	$(silox)_3Ta(\eta^2\text{-}C_2Me_2)$
66b	R = Me	68	$(silox)_3TaH_2$
69a	$[(silox)_2MH_2]_2$ M = Nb	70	$[(silox)_2TaCl]_2(\mu\text{-}H)_2$
69b	M = Ta	71	$(silox)_3Ta(\eta^2\text{-}CH_2O)$
72	$(silox)_3Ta(Et)H$	73	$(silox)_3Ta[\eta^2(N,C)\text{-}NC_5H_5]$ §
74	$[(silox)_3Ta]_2[\mu\text{-}\eta^2(1,2){:}\eta^2(4,5)\text{-}C_6H_6]$ §	75	$(silox)_3TiCl$
		77	$(silox)_3Ti$
76	$(silox)_3Ti(DME)$		
78a	$(silox)_3Ti\text{-}O\text{-}\dot{C}(C_6H_4R)$ R = H	79	$(silox)_3Ti\text{-}OCHPh_2$
78b	R = Me	80	$(silox)_3Ti\text{-}O(Ph)_2C\text{-}(H)\text{-}\overline{C(CH)_2C(CH{=}CH)}{=}CPhO\text{-}Ti(silox)_3$
81	$(silox)_3Ta{=}C{=}C{=}O$	82	$(silox)_3Sc(THF)$
83	$(silox)_3ScNH_3$	84	$(silox)_3V(THF)$

§ - crystal structure published.

Table 4 - Continued.

85a		R' = H R = H		
85b		R' = H R = Me		
85c		R' = H R = Et		
85d		R' = Me R = Me		
86a		R = H	87	$[(silox)_3Ti]_2(\mu\text{-}C_2H_4)$
86b		R = Me		
86c		$R = CF_3$		
88a		R = H		
88b		R = Me		
89			90	
91			92	
93a	$(silox)_3M(py)$	M = Sc	94	$(silox)_3Ti(2\text{-}NC_5H_4Me)$ ¶
93b		M = V		
93c		M = Ti		

¶ - crystal structure published.

The silox-containing transition metal complexes proved to be extremely robust, for example, 54 was heated at 200 °C for 7 days without noticeable decomposition. The undesirable displacement of silox by alkyllithiums during the preparations was not encountered, even though the R_3SiO^- moiety may be a reasonable leaving group due to charge stabilisation *via* the silicon.[51]

The reactivity of the silox complexes with small molecules has been investigated and, specifically, the reactivity of $(silox)_3Ta$, 62, has undergone intense scrutiny. This low valent, low co-ordinate early transition-metal complex is a potent reductant that can cleave carbon monoxide under mild conditions (< 1 atm, ~ 5 °C), yet does not bind common σ-donors such as phosphines or ethers.[52] The cleavage reaction provided an oxo complex, $(silox)_3Ta{=}O$ (63) and a dicarbide, $[(silox)_3Ta]_2(\mu\text{-}C_2)$ (64). Physical, theoretical and mechanistic investigations were subsequently reported by Neitheimer *et al.*.[56] Reactions of $(silox)_3Ta$ with other small molecules included dihydrogen, dioxygen, ethene, propene, 2-butyne and $(CH_2O)_n$.[52]

Another interesting study reported by Neitheimer *et al.*[54] yielded pyridine (η^2) and benzene [μ-$\eta^2(1,2)$:$\eta^2(4,5)$] adducts of $(silox)_3Ta$ (73 and 74). Of note was the uncommon mode of binding which disturbed the aromaticity of the fragment, yet fell short of utilising the hydrocarbon's full complement of π-electrons. An extended Hückel molecular orbital (EHMO) analysis of 62 was presented to provide a rationale for the behaviour of the molecule towards σ-donors and ligands with the capability to function as π-acids.[57]

Further, Covert and Wolczanski[55] described the use of the sterically demanding silox ligand to shield a reactive fragment within the hydrocarbon shell (78a, 78b). This involved the preparation of a diphenylcarboxyl radical derived from Ti(III) reduction

of benzophenone and the reversible C–C bond formation that accompanied its dimerisation (80).

Objectives of this work

From the foregoing survey of some of the main research areas and directions of organosilicon chemistry, it seems clear that there is a great deal of interest in using organosilicon metal complexes to model the interaction of catalytically important metals with silica surfaces. We chose to investigate the interactions of a bulky silanol, *n*-Bu_3SiOH, with compounds of some early transition metal elements such as Ta, Mo, Ti and Zr, in the hope that new tri-*n*-butylsiloxy complexes of these metals would be synthesised in which the three C_4 chains would provide a kind of hydrocarbon 'anchor' for the siloxy group. Similar reactions using the tertiary butyl derivative *t*-Bu_3SiOH ('silox') have been reported,[57] and we wished to investigate the corresponding *n*-butyl compounds.

As will be seen in the following chapter (Results and Discussion), the products of these reactions proved largely intractable, and so attention was switched to the corresponding complexes of the less sterically demanding phenyl derivatives, Ph_3SiOH and $Ph_2Si(OH)_2$. Here more success was achieved, with the synthesis of compounds such as $Cp_2Zr(OSiPh_3)_2$, $Cp_2TiCl(OSiPh_3)$ and the interesting spiro-compound $\overline{Ti[OSiPh_2(OSiPh_2)_3O]}_2$, upon which a full X-ray crystal structure was performed (Chapter 3 - X-Ray Crystallography). All of the detailed experimental methods and procedures, as well as the complete analytical and spectroscopic data, are reported in Chapter 4 - Experimental.

Chapter Two

Results and Discussion

CHAPTER 2
RESULTS AND DISCUSSION

Firstly, reactions involving tri-*n*-butylsilanol (*n*-Bu_3SiOH) will be discussed, which include several methods of preparation of this potential ligand, attempted preparations of tri-*n*-butylsiloxy salts, and reactions between *n*-Bu_3SiOH and selected early transition metal complexes, some of which involve the use of a base triethylamine, (Et_3N).

Secondly, reactions involving triphenylsilanol (Ph_3SiOH) will be discussed, which include the preparation of the sodium salt of Ph_3SiOH and reactions between Ph_3SiOH and selected early transition metal complexes in the presence of the base, Et_3N.

Finally, one more reaction will be discussed which involves diphenylsilanediol, $Ph_2Si(OH)_2$, and tetra-*n*-butoxytitanium. This yielded a most interesting spiro-complex, the crystal and molecular structure of which are discussed in Chapter 3 – X-Ray Crystallography.

The experimental procedures and analytical results are described in detail in Chapter 4 – Experimental.

Reactions involving tri-*n*-butylsilanol (*n*-Bu_3SiOH)

n-Bu_3SiOH was not available from any commercial supplier and two different methods were investigated for its synthesis. The first involved reacting neat *n*-Bu_3SiH with silver nitrate under an inert atmosphere, similar to the preparation described by Duffaut *et al.* (see Eqn 1).[25]

$$n\text{-}Bu_3SiH(l) + AgNO_3(s) \longrightarrow n\text{-}Bu_3SiOH(l) + Ag(s) + NO_2(g)$$

(Equation 1)

The literature reaction[25] involved the use of diethyl ether as the solvent. The preparation of tri-*t*-butylsilanol, *t*-Bu_3SiOH, was reported by Dexheimer and Spialter[22] and involved reacting neat *t*-Bu_3SiH with $AgNO_3$ in the absence of a solvent. The preparation of *n*-Bu_3SiOH was thus investigated in the absence of a solvent. The yellow/brown gas, NO_2, was evolved as the reaction commenced and the reaction reached completion after about 48 hours when bubbling had ceased. The crude product was separated from the silver metal by extraction with hexane, which was later removed under reduced pressure. Duffaut *et al.*[25] reported the formation of hexa-*n*-butyldisiloxane, (*n*-$Bu_3Si)_2O$, with a boiling point of 190–200 °C, as a by-product. A carefully-controlled vacuum distillation was considered to be the most suitable method for separation of the *n*-Bu_3SiOH from this by-product. A Kugelrohr vacuum distillation was used to separate the *n*-Bu_3SiOH from the crude product. Two distinct fractions were collected and were identified as *n*-Bu_3SiOH and (*n*-$Bu_3Si)_2O$ by their characteristic ^1H NMR spectra. The first fraction showed a typical broad singlet at δ 1.60 ppm integrating for one proton and corresponding to the hydroxy proton of *n*-Bu_3SiOH. The spectrum was unchanged when a D_2O wash was performed, indicating that the rate of exchange of the hydroxyl proton was slow. This singlet was absent in the spectrum of the second fraction, indicating the absence

of the hydroxyl proton. Both fractions showed three multiplets around δ 0.8 ppm which are typical for butyl protons. In neither case was the heptet expected around δ 3.7 ppm for the silyl proton of the starting material *n*-Bu_3SiH observed. The ^1H NMR spectra are reported in more detail in Chapter 4 – Experimental.

The boiling points observed were 90 °C (at 1 mmHg) for *n*-Bu_3SiOH and greater than 130 °C (at 2 mmHg) for (*n*-$Bu_3Si)_2O$. The literature boiling points[25] for *n*-Bu_3SiOH and (*n*-$Bu_3Si)_2O$ are 140–141 °C and 190–200 °C (at 760 mmHg), respectively, indicating a correlation between the experimentally observed and the literature values. The literature boiling point[62] for *n*-Bu_3SiH (at 760 mmHg) is 225–226 °C. The C, H microanalysis results were unsatisfactory (*i.e.* greater than 0.5 % difference between observed and expected values – up to 2.2 % difference for C). Technical problems were experienced with the microanalysis instrumentation which would account for the deviation from the expected values, as the ^1H NMR spectra certainly indicated that the separated products were pure.

This preparation was performed five times with the best yields being 56.0 % for *n*-Bu_3SiOH and a corresponding 9.2 % for (*n*-$Bu_3Si)_2O$.

The second method of preparation of *n*-Bu_3SiOH involved reacting *n*-Bu_3SiCl with potassium hydroxide in ethanol (see Eqn 2). Weidenbruch *et al.*[23] described the preparation of tri-*t*-butylsilanol, *t*-Bu_3SiOH from *t*-Bu_3SiCl using KOH in ethanol. A yield of 82 % was reported, so an analogous reaction involving *n*-Bu_3SiCl was investigated.

$$n\text{-}Bu_3SiCl(l) + KOH(s) \xrightarrow{EtOH} n\text{-}Bu_3SiOH(l) + KCl(s)$$

(Equation 2)

It was evident that the reaction had commenced, since potassium chloride, a white precipitate, formed in the reaction vessel. The reaction was allowed to continue for 48 hours, after which time the ethanol was evaporated and the crude product was extracted from the KCl using hexane. Kugelrohr vacuum distillation was again used to separate the products; two products were obtained and as above were identified as n-Bu_3SiOH and $(n\text{-}Bu_3Si)_2O$ from their ^1H NMR spectra. Peaks corresponding to ethanol were observed in the ^1H NMR spectrum of n-Bu_3SiOH and these were still evident after repeated distillations. The ratio of n-Bu_3SiOH to ethanol for all the samples ranged from 7 : 1 to 11 : 1 and remained unchanged after careful distillation. It may be that some form of hydrogen-bonded complex is formed between the n-Bu_3SiOH and ethanol, making the ethanol difficult to remove. The best yields obtained from three preparations were 84.9 % for n-Bu_3SiOH and 1.6 % for the $(n\text{-}Bu_3Si)_2O$.

Because of the ethanol contamination found in the latter procedure, only the n-Bu_3SiOH from the former method of preparation was used in further reactions between n-Bu_3SiOH and early transition metals. This was despite the greater yield of the latter procedure.

In a first attempt to prepare a salt of n-Bu_3SiO^-, n-Bu_3SiOH was reacted with sodium hydride, NaH, in THF at low temperatures and under an inert atmosphere (see Eqn 3).

$$2\,n\text{-}Bu_3SiOH\,(l) \;+\; 2\,NaH\,(s) \xrightarrow{THF} 2\,Na^+(OSiBu^n_3)^- + H_2\,(g)$$

(Equation 3)

A similar method of preparation was reported for the preparation of the *tert*-butyl analogue, $Na^+(OSiBu^t_3)^-$, by LaPointe *et al.*.[51] Evolution of a gas, presumably H_2,

was observed as the NaH was added. The reaction was allowed to continue for 1 day, and the crude product was separated from the excess NaH and the solvent. After repeated attempts to recrystallise the oily product, water and ethanol was the only solvent combination that produced any crystalline material.

No conclusion could be drawn about the identity of the product as the various analyses were confusing: the microanalyses were approximately one fifth of the expected values [*i.e.* for $Na^+(OSiBu^n_3)^-$]. There were no butyl peaks in the ^1H NMR spectrum, but peaks were observed which are characteristic of ethyl protons at δ 1.04 (t) and δ 3.50 ppm (q). The product is presumably chiefly NaOH and $Na^+(OCH_2CH_3)^-$, which would account for the strange analytical results. This method of preparation of a salt of *n*-Bu_3SiO^- was not pursued as the reaction between *n*-Bu_3SiOH and *n*-BuLi was also investigated with the aim of producing lithium tri-*n*-butylsilanoate, $Li^+(OSiBu^n_3)^-$.

The preparation of $Li^+(OSiBu^t_3)^-$ was reported by Lubben *et al.*[58] and a similar experimental procedure was investigated with the aim of preparing the *n*-butyl analogue, $Li^+(OSiBu^n_3)^-$. *n*-Bu_3SiOH was reacted with *n*-BuLi in hexane at -78 °C under an inert atmosphere (see Eqn 4).

$$n\text{-}Bu_3SiOH(l) + n\text{-}BuLi \xrightarrow{\text{hexane}} Li^+(OSiBu^n_3)^- + n\text{-}BuH(g)$$

(Equation 4)

After 24 hours no precipitation had occurred. A wet, white powder remained after the solvent had been removed under reduced pressure. The solid material was washed with hexane and after drying the various analyses were once again confusing. The ^1H NMR spectrum indicated the presence of *n*-Bu_3SiOH as the hydroxyl proton and butyl peaks were present and they integrated for the correct number of protons.

The microanalysis results were far from the expected values for either *n*-Bu_3SiOH or $Li^+(OSiBu^n_3)^-$. No further analytical tests were performed because of the apparent failure of the reaction. The white solid was presumably LiOH and the wetness observed after the reaction due to *n*-Bu_3SiOH; this would explain the analytical results.

At this stage further attempts to prepare a salt of *n*-Bu_3SiO^- were not pursued and the subsequent reactions with early transition metal compounds involved only *n*-Bu_3SiOH.

The first of a series of reactions between *n*-Bu_3SiOH and early transition metals to be attempted was that between *n*-Bu_3SiOH and $TaCl_5$. The aim was to substitute as many chlorine atoms with the tri-*n*-butylsiloxide ligand as possible (see Eqn 5).

$$TaCl_5(s) + x\ n\text{-}Bu_3SiOH(l) \longrightarrow TaCl_{5-x}(OSiBu^n_3)_x + x\ HCl(g)$$

(Equation 5)

LaPointe *et al.*[51] successfully prepared the *tert*-butyl compound, $(Bu^t_3SiO)_2TaCl_3$ from $TaCl_5$ and $Na^+(OSiBu^t_3)^-$. The sodium salt of *n*-Bu_3SiOH was not isolated (see above). As $TaCl_5$ is very reactive, an attempt was made to react neat *n*-Bu_3SiOH with $TaCl_5$. The reaction was performed under an inert atmosphere and stirred at room temperature for two hours after which it was refluxed for 3 days at 135 °C. The resultant solid material was filtered and washed with hexane.

The melting point of the solid was found to be greater than 350 °C. It was thought that the solid was tantalum pentoxide, Ta_2O_5, which has a literature melting point of 1800 °C.[63] A small portion of this material was placed in a crucible and heated intensely over a Bunsen burner to test for the the presence of carbon. Initially, the

white material darkened to a light brown colour but later became white again and remained this way with intense heating. This would indicate a predominantly non-carbon compound with only traces of carbon. The C and H microanalyses indicated no carbon or hydrogen. The solid white material was assumed to be Ta_2O_5.

The hexane was removed from the filtrate obtained above, leaving an oil which was shown to comprise mainly (n-$Bu_3Si)_2O$ and n-Bu_3SiOH with traces of some other product (as indicated by TLC), presumably the desired tantalum product, $TaCl_{5-x}(OSiBu^n{}_3)_x$. Attempts to isolate and ascertain the nature of this product were not pursued because of the poor yield. The ^1H NMR spectrum showed the presence of butyl proton resonances with an hydroxyl proton present in a small proportion [*ca.* ratio 1 : 4, n-Bu_3SiOH : (n-$Bu_3Si)_2O$]. The microanalysis results were unsatisfactory as the oil was neither purified nor homogeneous. A possible explanation for the poor reactivity of the n-Bu_3SiOH is that the (n-$Bu_3Si)_2O$ dimer is readily formed when the n-Bu_3SiOH is heated in the presence of $TaCl_5$, thus leaving the $TaCl_5$ unreacted and susceptible to reaction with oxygen or moisture during the reaction or work-up. This was investigated and is discussed later.

Takiguchi and Suzuki[39] described the use of the base, triethylamine (Et_3N), as a hydrogen acceptor in the preparation of some triorganosiloxy derivatives of bis(cyclopentadienyl)titanium dichloride using R_3SiOH. The reaction between $TaCl_5$ and n-Bu_3SiOH was repeated using this base as a hydrogen chloride acceptor, with the aim of facilitating the formation of the $TaCl_{5-x}(OSiBu_3{}^n)_x$ complex (see Eqn 6).

$$x\ n\text{-}Bu_3SiOH(l) + TaCl_5(s) + x\ Et_3N(l) \xrightarrow{C_6H_6} TaCl_{5-x}(OSiBu^n_3)_x + x\,Et_3NH^+Cl^-(s)$$

(Equation 6)

Benzene was used as the solvent and when the base was added, a reaction was immediately evident. The reaction was allowed to continue for three hours after which the solid white precipitate was filtered and was shown to contain $Et_3NH^+Cl^-$. The ^1H NMR spectrum showed a multiplet and a triplet at δ 3.08 and δ 1.44 ppm respectively corresponding to the ethyl protons and a broad peak at δ 1.65 ppm corresponding to the hydrochloride proton. A viscous, yellow oil was recovered from the filtrate. The ^1H NMR spectrum of this oil indicated mainly *n*-Bu_3SiOH and (*n*-$Bu_3Si)_2O$, but the TLC of this crude product revealed that a positive reaction had indeed occurred, although only to a limited extent. As in case above, the trace product was not isolated or characterised. Presumably most of the $TaCl_5$ or its decomposition products formed an admixture with the $Et_3NH^+Cl^-$.

The literature melting point of triethylamine hydrochloride is reported to be 261 °C (dec.).[62] This was not observed for the product of the above reaction (or of any other subsequent reactions where Et_3N was used as the hydrogen chloride acceptor). The ^1H NMR spectrum and microanalyses clearly indicated $Et_3NH^+Cl^-$. The microanalyses, in some cases, differed significantly from the expected values because the triethylamine hydrochloride products were not purified, as their presence merely indicated the occurrence of the reaction and may well have been contaminated with insoluble by-products of the reaction. This is particularly notable in the case of both of the $TaCl_5$ reactions with *n*-Bu_3SiOH and Ph_3SiOH. Table 1 shows the relevant results for all reactions where Et_3N was used. The agreement between the experimentally observed melting points is irrefutable and clearly indicates that the same compound had been obtained from each reaction. The apparent discrepancy between the experimental and literature melting points prompted the preparation of $Et_3NH^+Cl^-$. Triethylamine was reacted with concentrated hydrochloric acid and the resulting product was recrystallised from ethanol by cooling to 0 °C. The melting point of this product (194–197 °C sublim.) was identical to those observed

Table 1 - Selected data from all reactions involving Et_3N as the hydrogen chloride acceptor.

Reagents	Solvent used	^{1}H NMR δ (ppm)			Microanalysis †			Melting Point (°C)
(see key below)		$(CH_3CH_2)_3NH^+Cl^-$	$(CH_3CH_2)_3NH^+Cl^-$	$(CH_3CH_2)_3NH^+Cl^-$	C(%)	H(%)	N(%)	
I - lit.[64]	alcohol	-	-	-	-	-	-	253–254, sublimes at 245
II + III	ethanol	-	-	-	-	-	-	194–197 sublim.
IV + V + II	benzene	1.40	1.65	3.08	19.0	5.7	3.5	196–199 sublim., some remained < 600
VI + V + II	no solvent	1.40	1.92	3.11	36.2	8.6	6.8	193–197 sublim.
VII + V + II	benzene	1.38	1.90	3.07	52.2	10.8	10.5	195–198 sublim.
VII + V + II	THF	1.38	1.88	3.08	53.6	11.0	10.0	196–199 sublim.
IV + IX + II	benzene	-	-	-	36.5	8.0	7.1	194–197 sublim., some remained < 600
VII + IX + II	benzene	1.38	1.90	3.07	52.9	11.3	10.4	195–197 sublim.
VIII + IX + II	benzene	1.38	1.88	3.08	56.0	9.8	7.4	slight melting 147–150, 194–197 sublim.
X + IX + II	benzene	1.37	1.97	3.07	52.6	11.5	10.0	194–197 sublim.

Key: I - literature[64] IV - $TaCl_5$ VII - Cp_2TiCl_2 X - $Cp^*_2ZrCl_2$
II - Et_3N V - n-Bu_3SiOH VIII - Cp_2ZrCl_2
III - HCl VI - $MoCl_5$ IX - Ph_3SiOH

† - The calculated CHN values for $Et_3NH^+Cl^-$ are 52.4, 11.7 and 10.4 % respectively.

experimentally. The Merck Index[64] reported the melting point of $Et_3NH^+Cl^-$ from alcohol as 261 °C (dec.), so the possibility of a polymorphic difference expaining the discrepancy should be ruled out.

A reactant similar to the $TaCl_5$ was used in the next reaction attempted when $MoCl_5$ was reacted with neat *n*-Bu_3SiOH in the presence of the base, Et_3N. This reaction was carried out under an inert atmosphere because of the reactivity of $MoCl_5$ with moisture and oxygen, with an aim similar to that of the $TaCl_5$ reactions (see Eqn 7).

$$x\ n\text{-}Bu_3SiOH(l) + MoCl_5(s) + x\ Et_3N(l) \longrightarrow MoCl_{5-x}(OSiBu^n_3)_x + x\ Et_3NH^+Cl^-(s)$$

(Equation 7)

As in the previously described reaction involving $TaCl_5$, an immediate reaction was observed when the base was added. A cloudiness appeared above the reaction solution which gradually dispersed. The $MoCl_5$ disappeared after a few minutes and the reaction was terminated after 60 hours. The small deposit in the reaction vessel was filtered, but during the filtration process a second intensely blue precipitate formed in the filtrate. Even with careful filtration (when the reaction was repeated) using an imperfect nitrogen atmosphere, the precipitate once again formed immediately. A suitable nitrogen-atmosphere filtration apparatus was not available so the reaction could not be investigated any further, as exclusion of all traces of oxygen and nitrogen could not be guaranteed.

The blue precipitate was filtered and washed with benzene. The solvent was removed from the filtrate under reduced pressure and a viscous, yellow oil remained. The oil was investigated and TLC revealed a mixture of starting materials and products. Besides the *n*-Bu_3SiOH and (*n*-$Bu_3Si)_2O$ the other components were

present in trace amounts. One of these trace products was presumably the desired complex, $MoCl_{5-x}(OSiBu^n_3)_x$. As above, the oil was not purified because of the poor yields. The ^1H NMR spectrum indicated a result similar to that previously observed, *i.e.* predominantly a mixture of *n*-Bu_3SiOH and (*n*-$Bu_3Si)_2O$ (*ca.* 1 : 1).

The intensely blue precipitate that formed during the filtration process was presumed to be molybdenum blue (first discovered by Berzelius in 1826).[65] Several distinct substances are included under this common name, but $Mo_8O_{23}.xH_2O$ generally appears to satisfy the analyses. Molybdenum blues are formed by the oxidation of pentavalent molybdenum (*cf.* $MoCl_5$) with water[65] or reduction of MoO_3 by Cu and HCl, Zn, Al, Fe, hydrazine, H_2S, *etc.*.[66] Evaporation of the deep blue colloidal liquid gives a glassy, black residue, which cannot be completely dried as it decomposes above 100 °C into MoO_2 and MoO_3, but can recombine at a lower temperature.[67]

The unsuccessful reactions between the tri-*n*-butylsilanol and the MCl_5 (M = Ta or Mo) appear to be due to the formation of the dimer, (*n*-$Bu_3Si)_2O$. In an attempt to verify the assumption that heating and the use of the base promoted the formation of (*n*-$Bu_3Si)_2O$, a separate experiment was performed. Neat *n*-Bu_3SiOH was refluxed in an inert atmosphere for 48 hours. A small sample of the liquid was removed for ^1H NMR analysis, which revealed that the *n*-Bu_3SiOH was unchanged. The base, Et_3N, was added and the mixture was refluxed for a further 24 hours. The ^1H NMR indicated unreacted *n*-Bu_3SiOH and Et_3N. Neither $Et_3NH^+Cl^-$ nor (*n*-$Bu_3Si)_2O$ was observed. The formation of the (*n*-$Bu_3Si)_2O$ dimer is thus reliant on the presence of the $TaCl_5$ or $MoCl_5$.

The readily formed metal oxides (Ta_2O_5 and $Mo_8O_{23}.xH_2O$) also significantly affect the formation of the desired metal siloxide. The tantalum pentoxide seemed to form

during the reaction process and the molybdenum blue formed during the filtration of the triethylamine hydrochloride component.

The products from the previous reactions between *n*-Bu_3SiOH and MCl_5 (M = Ta or Mo) were clearly extremely air-sensitive. Due to the lack of specialised equipment necessary to cope with the experimental techniques required, less reactive reagents and thus products were sought. The bis-cyclopentadienyl dichloride metal complexes, Cp_2MCl_2 (M = Ti or Zr), were selected as they would be less air-sensitive, provide more tractable products, and, because of the bulk of the *n*-butyl groups, would likely yield an interesting molecular structure for crystallographic studies (see Eqn 8).

$$2\,n\text{-}Bu_3SiOH(l) + Cp_2MCl_2(s) + 2\,Et_3N(l) \xrightarrow{C_6H_6} Cp_2M(OSiBu^n{}_3)_2 + 2\,Et_3NH^+Cl^-(s)$$

(M = Ti, Zr)

(Equation 8)

The preparation of some triorganosiloxy derivatives of bis(cyclopentadienyl)titanium dichloride using R_3SiOH was reported by Takiguchi and Suzuki.[60] Their work involved using triphenylsilanol (Ph_3SiOH), diphenylmethylsilanol ($Ph_2MeSiOH$), dimethylphenylsilanol ($Me_2PhSiOH$) and diphenylbutylsilanol ($Ph_2BuSiOH$). It therefore seemed pertinent to investigate the reaction between *n*-Bu_3SiOH and Cp_2TiCl_2, and to extend the investigation to the reaction with Cp_2ZrCl_2.

The reaction between *n*-Bu_3SiOH and bis(cyclopentadienyl)titanium dichloride (or titanocene dichloride), Cp_2TiCl_2, was carried out at room temperature under an inert atmosphere initially without a solvent and when no reaction was evident benzene was added. The reaction only commenced when the base, Et_3N, was added. The solution

was refluxed for 1 hour and was then stirred at room temperature overnight. The white precipitate was filtered and was shown by microanalysis, ^{1}H NMR spectroscopy, and melting point to be $Et_3NH^+Cl^-$.

The solvent was removed from the filtrate but little success was achieved trying to recrystallise the viscous, orange oil. When methanol was added to the oil, the orange-coloured component appeared to separate into the methanol. ^{1}H NMR spectrum indicated that the remaining viscous oil was $(n\text{-}Bu_3Si)_2O$ with the characteristic peaks at δ 0.57, δ 0.88 and δ 1.31 ppm. Two small peaks were observed at δ 6.22 and δ 6.43 ppm and were assumed to be traces of either the starting material (Cp_2TiCl_2) or a cyclopentadienyl-containing product.

Strangely, once the methanol had been evaporated from the orange component, the remaining red deposit became insoluble in all solvents except DMSO, in which it was only partially soluble. Recrystallisation from this solvent was not achieved. Even though the product was not finally purified various analyses were performed. The product did not appear to be the intended product [*i.e.* $Cp_2Ti(OSiBu^n{}_3)_2$] as the C and H elemental microanalyses were low. The ^{1}H NMR spectrum revealed that the red product contained a large proportion of butyl protons (*i.e.* at δ 0.45, δ 0.80 and δ 1.21 ppm). It was assumed that these corresponded chiefly to the disiloxane derivative, $(n\text{-}Bu_3Si)_2O$. Two small sets of peaks were located further downfield at δ 3.07 (3 H, m) and δ 3.15 (2 H, s) ppm. We had hoped that these peaks might have indicated the formation of an η^1-cyclopentadienyl-containing compound, but the spectrum did not show the required 2 : 2 : 1 ratio of peaks associated with an η^1-bonding cyclopentadienyl group. They also did not correspond to the chemical shifts normally observed for η^5-cyclopentadienyl groups. Unfortunately the red product could not be separated from the $(n\text{-}Bu_3Si)_2O$ because of it poor solubility and its small yield, and this reaction was not investigated any further.

Similarly, the zirconocene dichloride, Cp_2ZrCl_2 was reacted with *n*-Bu_3SiOH under an inert atmosphere, using Et_3N as the base (see Eqn 8). THF was the solvent used and when the base was added an immediate reaction was evident as the solution rapidly appeared to become a thick gel. This was diluted with more THF, revealing that it was simply a thick suspension. After the system had stirred overnight the suspension was filtered. The isolated solid was shown by microanalysis and ^1H NMR spectroscopy to be $Et_3NH^+Cl^-$.

The THF was evaporated from the filtrate, leaving a viscous oil. The oil was not purified but analyses were performed. The ^1H NMR spectrum revealed peaks typical of butyl protons at δ 0.57 (m), δ 0.91 (m) and δ 0.32 ppm (m). A singlet was also observed at δ 6.24 ppm which was tentatively assigned to the Cp protons of $Cp_2Zr(OSiBu^n_3)_2$, as the singlet corresponding to Cp_2ZrCl_2 is normally found at δ 6.49 ppm. This peak integrated for only one proton whereas the peaks assigned to the butyl protons integrated for 27 protons. This would indicate that the viscous oil was predominantly (*n*-$Bu_3Si)_2O$ containing a small amount of the desired product, bis(cyclopentadienyl)bis(tri-*n*-butylsiloxy)zirconium(II), $Cp_2Zr(OSiBu^n_3)_2$.

At this stage it was realised that the reactions with *n*-Bu_3SiOH were all resulting in products (if any) that were intractable in our hands. The lack of success using this potential ligand might have been due to its large size, the steric bulk of the three *n*-butyl groups hindering effective coordination to metal centres. It may also, or alternatively, be that the presence of the three 'floppy' C_4 chains resulted in products that were non-crystalline or even oils, making their separation and purification difficult. There is no doubt that it was difficult in these reactions to prevent formation of hexa-*n*-butyldisiloxane, (*n*-$Bu_3Si)_2O$, and that any more desirable products were only present in small quantities, if at all.

Attention was therefore turned to a corresponding set of reactions using the less sterically demanding phenyl analogue, Ph_3SiOH.

Reactions involving Ph_3SiOH

In view of the large number of organometallic and coordination complexes containing the triphenylsiloxy ligand reported in the literature (see, for example, refs 36–38, 42, 43, 68–70), it was felt that similar reactions to those attempted earlier using the tri-*n*-butyl derivative might meet with more success when using the less sterically demanding Ph_3SiOH.

As was done for *n*-Bu_3SiOH, attempts were made to prepare a salt of Ph_3SiO^-. The preparation of sodium triphenylsilanoate, $Na^+(OSiPh_3)^-$, was reported by Hyde *et al.*[33] from the reaction of Ph_3SiOH with NaH. In a similar way Ph_3SiOH was reacted with NaH in THF at -78 °C under an inert atmosphere (see Eqn 9).

$$2\ Ph_3SiOH(s)\ +\ 2\ NaH(s) \xrightarrow{THF} 2\ Na^+(OSiPh_3)^-(s)\ +\ H_2(g)$$

(Equation 9)

As the system was allowed to warm a gas, presumably H_2, was evolved. After 20 hours, the NaH was separated from the solution and the THF was evaporated under reduced pressure leaving a white powder. This was recrystallised from ethanol to give what appeared to be sodium triphenylsilanoate, although the microanalysis results were unsatisfactory. Only a multiplet at δ 7.4 ppm in the ^1H NMR spectrum was observed, corresponding to the phenyl protons and consistent with $Na^+(OSiPh_3)^-$. The characteristic broad singlet in the region of δ 2.5 ppm corresponding to the hydroxyl proton of Ph_3SiOH was not observed. As reported by Hyde *et al.*,[33] no melting was observed below 600 °C. The yield of 5.5 % was unsatisfactory so another recrystallisation was carried out on solid recovered from the filtrate. The various analytical results were better than those of the first product (satisfactory C, H microanalysis results), but the yield was also very poor (6.6 %).

Even though the preparation of the sodium salt of Ph_3SiOH was successful, the yields were so poor that it would have been impractical to perform reactions involving the salt. As was done in the case of *n*-Bu_3SiOH, the Ph_3SiOH was used as such in subsequent reactions and Et_3N was used as a hydrogen chloride acceptor.

As Ph_3SiOH, unlike *n*-Bu_3SiOH, forms stable metal complexes, it was thought that the product formed from the reaction with $TaCl_5$ would be more stable than the product from the analogous *n*-Bu_3SiOH reaction. The product from the proposed reaction was also expected to be a solid, which would facilitate its isolation and purification (see Eqn 10).

$$x\,Ph_3SiOH(s) + TaCl_5(s) + x\,Et_3N(l) \xrightarrow{C_6H_6} TaCl_{5-x}(OSiPh_3)_x + x\,Et_3NH^+Cl^-(s)$$

(Equation 10)

In a first experiment, Ph_3SiOH was reacted with $TaCl_5$ in benzene with Et_3N as the base. The mixture was refluxed for 48 hours, after which the precipitate was filtered and washed with benzene. This was analysed and appeared to be $Et_3NH^+Cl^-$ contaminated with $TaCl_5$ (or Ta_2O_5). The characteristic sublimation of $Et_3NH^+Cl^-$ was clearly observed between 194 and 197 °C, but some material remained unmelted below 600 °C (the limit of the melting point instrument). ^1H NMR spectroscopy was not possible as the precipitate was heterogeneous and one of the components was insoluble in all of the appropriate solvents. When the solid that was recovered from the filtrate was analysed, it appeared to be Ph_3SiOH. The melting point indicated Ph_3SiOH and the ^1H NMR spectrum was identical to the Ph_3SiOH starting material, although the microanalysis results were slightly unsatisfactory.

As the Ph_3SiOH was apparently recovered from the reaction unchanged, it was necessary to determine what reaction had occurred to form the $Et_3NH^+Cl^-$. $TaCl_5$ was reacted with Et_3N, under an inert atmosphere, in refluxing benzene for 16 hours. The insoluble solid white material that formed was filtered off and investigated. The melting point indicated that it was $Et_3NH^+Cl^-$, but some of the material remained unmelted up to 600 °C. The material was dissolved in dichloromethane and the insoluble component was filtered off and washed with CH_2Cl_2. The solvent was then evaporated from the filtrate. The melting point of the residue was observed to be characteristic of $Et_3NH^+Cl^-$, and the ^1H NMR spectrum revealed the peaks associated with $Et_3NH^+Cl^-$ [*i.e.* at δ 1.38 (t), δ 1.88 (br. s) and δ 3.08 ppm (m)]. The insoluble white component with melting point greater than 600 °C was assumed to be Ta_2O_5.

As $Et_3NH^+Cl^-$ was clearly formed as a product in the reaction between $TaCl_5$ and Et_3N, it would seem that some other component must have been present to facilitate this reaction. The most obvious explanation would be that the reaction mixture was somehow contaminated with trace amounts of water which reacted with the $TaCl_5$, the Et_3N in turn reacting with the hydrochloride species formed. As the solvents were all pre-dried, the water could have been present in the Et_3N, though this was stored over molecular sieves. The reaction was repeated, taking care to exclude all moisture, but the same two products were formed. At present we cannot explain the formation of the hydrochloride, assuming our experimental conditions to be moisture free. $TaCl_5$ was the most reactive species used in the series of reactions investigated and appeared to be the only reactant affected by possible moisture in the Et_3N. Therefore the only reactions possibly influenced by the trace moisture in the system were those between $TaCl_5$ and either *n*-Bu_3SiOH or Ph_3SiOH.

A different type of reaction was attempted for the reaction between Ph_3SiOH and $TaCl_5$. It was a solid state reaction where no solvent or base was used. Finely ground Ph_3SiOH and $TaCl_5$ were combined in a Schlenk tube and heated at 110 °C (at 4 mmHg) for 18 hours. A vacuum sublimation apparatus was used in an attempt to isolate the products from the starting materials. The sublimation attempt proceeded over two days at 110 °C and 0.25 mmHg. A small amount of product (0.02 g) was recovered from the cold finger and this analysed for Ph_3SiOH. The ^1H NMR spectrum showed both the phenyl and hydroxyl protons. The hydrogen microanalysis value was satifactory (*i.e.* only 0.2 % difference between observed and calculated values) but the carbon microanalysis value was not acceptable (*i.e.* 3.1 % out).

As was found for the *n*-Bu_3SiOH reactions, the products of the reactions between the silanol and the MCl_5 were too reactive and too difficult to isolate and identify, if they formed at all. The reactivity of $TaCl_5$ and other metal halides can be lessened by the introducion of a mono-η^5-cyclopentadienyl ligand. This can be achieved by a number of direct routes from the parent metal halide.[71–74] One such preparation employs organotin reagents, such as $CpSnR_3$ (R = H or Me), as mild and controllable sources of a single Cp ligand and was reported by Bunker *et al.*[72] (see Eqn 11).

$$MCl_5 + CpSnR_3 \longrightarrow CpMCl_4 + SnClR_3$$

(M = Nb or Ta, R = H or Me)

(Equation 11)

$CpTaCl_4$ might be used instead of $TaCl_5$ to react with either *n*-Bu_3SiOH or Ph_3SiOH, but this potential route for the preparation of metal siloxides was not investigated in this work.

Once again, as for the *n*-Bu_3SiOH reactions, the less reactive Cp_2MCl_2 (M = Ti or Zr) complexes were employed to react with the silanol. Noltes and van der Kerk[75] and Takiguchi and Suzuki[39] reported the preparation of triphenylsiloxy derivatives of bis(cyclopentadienyl)titanium dichloride. Noltes and van der Kerk[75] used sodium triphenylsilanoate and performed the reaction in toluene yielding bis(cyclopentadienyl)(triphenylsiloxy)titanium chloride, bis(cyclopentadienyl)-bis(triphenylsiloxy)titanium or tetrakis(triphenylsiloxy)titanium, under different reaction conditions. Takiguchi and Suzuki[39] described the preparation of bis(cyclopentadienyl)bis(triphenylsiloxy)titanium from triphenylsilanol and Cp_2TiCl_2 in THF using Et_3N as a hydrogen chloride acceptor. As for the *n*-Bu_3SiOH reactions, it thus seemed of interest to investigate the reactions between Ph_3SiOH and both Cp_2TiCl_2 and Cp_2ZrCl_2.

Ph_3SiOH was reacted with the Cp_2TiCl_2 in benzene under an inert atmosphere, using Et_3N as the base, with the aim that a reaction such as that depicted in Eqn 12 would occur.

$$2\ Ph_3SiOH(l) + Cp_2MCl_2(s) + 2\,Et_3N(l) \xrightarrow{C_6H_6} Cp_2M(OSiPh_3)_2 + 2\,Et_3NH^+Cl^-(s)$$

(M = Ti or Zr)

(Equation 12)

The solution changed from red to orange after 1 hour, and was refluxed for 2 days. The white precipitate was filtered off, washed and analysed. The various analyses performed indicated that this was $Et_3NH^+Cl^-$. The C, H microanalyses were satisfactory and the ^1H NMR spectrum showed the expected peaks.

The solvent was evaporated from the filtrate and the resultant orange-coloured solid was recrystallised from a minimum of hot toluene. The melting point was observed to be 173–174 °C and both the C, H microanalyses and the ^{1}H NMR spectrum indicated $Cp_2TiCl(OSiPh_3)$. The desired product, $Cp_2Ti(OSiPh_3)_2$, was not observed. This result was confirmed by mass spectroscopy which contained a peak corresponding to the parent molecular ion of 488. Strangely, peaks higher than 488 were also observed, *i.e.* 1072, 995, 917, 876, 718, 634 and 553. These peaks could not be assigned unambiguously and it was suspected that they could correspond to the dimer $[Cp_2TiCl(OSiPh_3)]_2$, bridged by the chloride group and the oxygen atom of the triphenylsiloxy ligand. Alternatively, the fragments may have recombined in the ionisation chamber to form heavier ions than the parent molecular ion at 488. Neither microanalysis nor ^{1}H NMR could be used to distinguish between the monomer and the dimer, while an attempt to determine the molecular mass using Rast's camphor method proved inconclusive.

The preparation of bis(cyclopentadienyl)bis(triphenylsiloxy)zirconium(IV) from dimethylzirconocene and triphenylsilanol in diethyl ether was reported by Babaian *et al.*.[42] As for Cp_2TiCl_2, bis(cyclopentadienyl)zirconium dichloride (or zirconocene dichloride, Cp_2ZrCl_2) was reacted with Ph_3SiOH in benzene under an inert atmosphere using Et_3N as a hydrogen chloride acceptor to prepare $Cp_2Zr(OSiPh_3)_2$ (see Eqn 12). The solution was refluxed for 2 days, after which the white precipitate was filtered off and washed. Various analyses once again indicated that $Et_3NH^+Cl^-$ had formed, although the microanalyses were slightly unsatisfactory. This was not considered a problem as the $Et_3NH^+Cl^-$ only indicated that the reaction had occurred, and purification was not required. Similarly, the melting point revealed an impure product, with initial melting observed between 147 and 150 °C (presumably unreacted Ph_3SiOH, lit.,[62] m.p. 153–155 °C) and sublimation of the remainder of the product observed between 194 and 196 °C, characteristic of $Et_3NH^+Cl^-$. The ^{1}H

NMR spectrum indicated the characteristic peaks for $Et_3NH^+Cl^-$ at δ 3.08, δ 1.88 and δ 1.38 ppm.

The desired product from the filtrate was recrystallised from hot dichloromethane. Various analyses indicated the successful synthesis of bis(cyclopentadienyl)-bis(triphenylsiloxy)zirconium(II), $Cp_2Zr(OSiPh_3)_2$. The ^1H NMR spectrum showed only the shifted phenyl protons at δ 7.32 ppm (from δ 7.41 ppm) and the shifted cyclopentadienyl protons at δ 6.03 ppm (from δ 6.49 ppm). XRF indicated the presence of both silicon and zirconium in the crystalline product. The homogeneous sample was ground to a fine powder, mounted, and irradiated with tungsten X-ray radiation to exhibit the observed fluorescences (see Figure 1). The K_α and K_β fluorescences were observed for the silicon present in the sample and the L_α and L_β for the zirconium present. This confirmed that zirconium was present in the product as the ^1H NMR was only of use to indicate the presence of the phenyls of the $(Ph_3SiO)^-$ species. Regrettably, the XRF method could not be used to obtain quantitative results (*i.e.* Zr : Si ratio). A yield of 80 % was achieved, and the C, H microanalysis values were satisfactory.

The literature[42] melting point of $Cp_2Zr(OSiPh_3)_2$ from toluene was reported to be 292–296 °C. The melting point observed by us for the product recrystallised from dichloromethane was 187–190 °C. If we accept the literature melting point for what it is, this discrepancy can be ascribed to the formation of different polymorphs of the same product as a result of the different solvents used for the recrystallisations.

X-Ray crystallography was performed on a few of the better-quality crystals. Regrettably, software failure or inadequacy resulted in the inability of the diffractometer to find the monoclinic unit cell determined by X-ray photographic

methods and thus data could not be collected for an X-ray structural study. (This is discussed in more detail later in Chapter 3 – X-Ray Crystallography.)

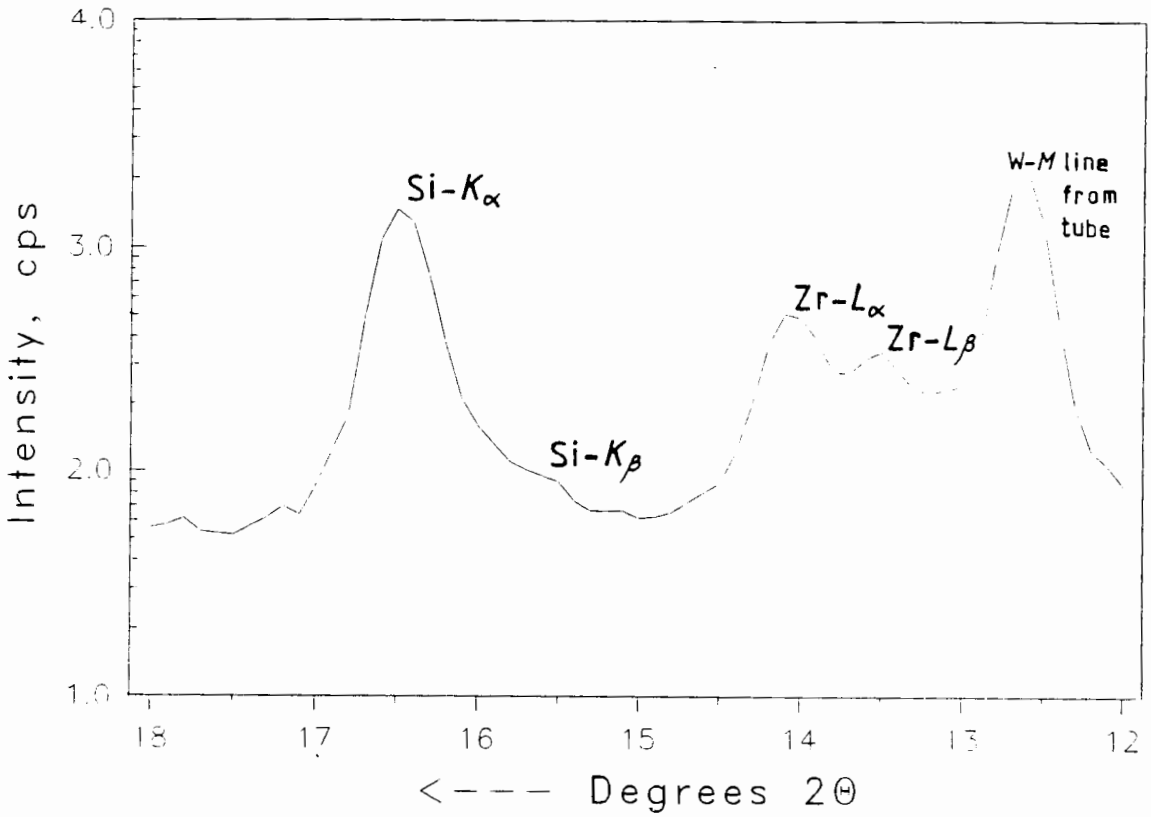


Figure 1 - XRF wavelength scan (2θ = 12 to 18 °) for $Cp_2Zr(OSiPh_3)_2$.

Next, a metal complex closely related to Cp_2ZrCl_2 was used with the aim of performing a crystallographic study on a triphenylsiloxy-containing metal complex. Bis(pentamethylcyclopentadienyl)zirconium dichloride, $Cp^*_2ZrCl_2$, was reacted with Ph_3SiOH in benzene under an inert atmosphere with the base, Et_3N (see Eqn 13).

$$2\ Ph_3SiOH(l) + Cp^*_2\ ZrCl_2(s) + 2\ Et_3N(l) \xrightarrow{C_6H_6} Cp^*_2\ Zr(OSiPh_3)_2\ (s) + 2\ Et_3NH^+Cl^-(s)$$

(Equation 13)

When the base was added there was no immediate reaction visible, so the solution was refluxed for 24 hours. During this time a precipitate formed, which was filtered off and the various analyses indicated that it was $Et_3NH^+Cl^-$; the microanalyses were satisfactory and the expected peaks were observed in the ^1H NMR spectrum. Preliminary analyses of the crude product indicated the presence of the desired product, $Cp^*_2Zr(OSiPh_3)_2$, which was evident from the ^1H NMR spectrum with a shifted peak at δ 1.79 ppm (from δ 1.96 ppm) for the methyl protons of the Cp^*.

Two attempts were made to recrystallise this material, which was dissolved in a minimum of dichloromethane to which a small volume of hexane was added. After cooling at -18 °C for two weeks, the crystals which had grown were separated from the mother liquor and washed with hexane. The crystals were manually separated into three groups whilst viewing under a microscope: white, non-crystalline material (m.p. 323–330 °C); white, non-crystalline material with clear crystals attached; and clear, crystalline material (charring from 180 °C, no melting below 600 °C). The yields were so low that there was only sufficient material to perform melting point measurements. A second attempt proved to be equally unsuccessful.

It was evident that the desired bis(pentamethylcyclopentadienyl)bis(triphenylsiloxy)-zirconium(II) had indeed been prepared, but regrettably it was not possible to purify it by recrystallisation methods.

As was mentioned earlier, Noltes and van der Kerk[75] reported the preparation of tetrakis(triphenylsiloxy)titanium as a by-product in the preparation of bis(cyclopenta-dienyl)bis(triphenylsiloxy)titanium. If crystals of $Ti(OSiPh_3)_4$ of suitable quality for X-ray crystal structure analysis could be grown, it was thought that a most interesting crystallographic structural study could result. Zeitler and Brown[76,77] described a more efficient preparation of the tetrakis(triphenylsiloxy)titanium, which involved

reacting triphenylsilanol with tetra-*n*-butoxytitanium, Ti(*n*-BuO)$_4$, either in benzene or without a solvent.

Ti(*n*-BuO)$_4$ was reacted with Ph_3SiOH in diethyl ether under an inert atmosphere (see Eqn 14).

$$4\,Ph_3SiOH(s) + Ti(n\text{-}BuO)_4(l) \xrightarrow{Et_2O} Ti(OSiPh_3)_4(s) + 4\,n\text{-}BuOH(l)$$

(Equation 14)

The reaction was spontaneous, which was evident from the white precipitate that formed. The reaction mixture was stirred overnight, after which the precipitate was filtered off and washed with diethyl ether. The product exhibited poor solubility properties, although it was observed to dissolve in boiling pyridine. A slow-cooling experiment was performed in an attempt to achieve crystallisation. The product was dissolved in a minimum amount of pyridine and was slowly cooled from 120 °C for 24 hours. No crystallisation was evident, so some of the solvent was allowed to evaporate. After a number of days, the volume had decreased slightly and closer inspection revealed that a gel had formed. Zeitler and Brown[75] reported that tetrakis(triphenylsiloxy)titanium exhibited poor solubility properties. Pyridine was the only solvent which dissolved the product satisfactorily. It was suspected that the $Ti(OSiPh_3)_4$ reacted with the pyridine to form a new coordination complex which might have later polymerised or formed a gel.

In a separate experiment, a different method of purifying the product in crystalline form was investigated. The sublimation temperature of the product was found to be ~ 380 °C at 1 mmHg. Zeitler and Brown[76] reported that vacuum sublimation at 370 °C was used to purify the product. Because of the temperature limitations of oil baths, an alternative method of regulated heating was employed in order to perform a

sublimation experiment. Holes were bored in a large cylindrical aluminium block to accommodate a cold finger sublimation tube and a thermocouple probe (see Figure 2).

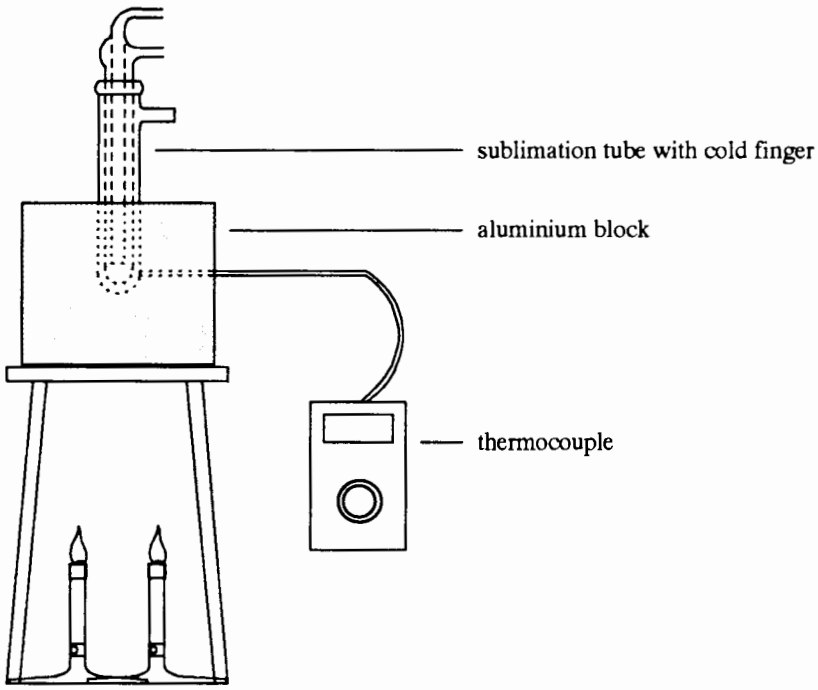


Figure 2 - The experimental arrangement used for the controlled, high temperature, vacuum sublimation.

Aluminium was selected because of its good thermal conductivity properties and because high temperatures could be carefully controlled. The block was heated using two Bunsen burners and in later experiments by a hot plate, while the whole apparatus was insulated by fire bricks (as used in furnaces). In a series of attempts, the product was successfully sublimed, but no crystalline material was produced, even with varied temperatures and durations of sublimation.

The sublimed products, even though not crystalline, were combined and various analyses were performed. The melting point and the C, H microanalyses indicated that the sublimed product was the desired tetrakis(triphenylsiloxy)titanium(IV), $Ti(OSiPh_3)_4$. ^1H NMR could not be used as a quantitative tool to confirm the molecular structure as the phenyl protons are the only proton-containing portion of the compound.

The aim of performing a crystallographic study on this product was not realised because of the inability to crystallise the product either from solution or by sublimation. Further studies on $Ti(OSiPh_3)_4$ were not performed.

The reactions using Ph_3SiOH turned out to be overall more successful than those using *n*-Bu_3SiOH, for although only starting material was recovered from the reaction with $TaCl_5$, pure samples of $Cp_2Zr(OSiPh_3)_2$, $[Cp_2TiCl(OSiPh_3)]_n$ (n = 1 or 2, see previous discussion) and $Ti(OSiPh_3)_4$ were obtained, while the pentamethylcyclopentadienyl derivative, $Cp^*_2Zr(OSiPh_3)_2$ was obtained, but in a quantity too small to purify satisfactorily. Disappointment at not obtaining crystals of $Ti(OSiPh_3)_4$ suitable for X-ray analysis, and the failure of the diffractometer to locate the same monoclinic unit cell as found from photographic methods for $Cp_2Zr(OSiPh_3)_2$ (see Chapter 3 – X-Ray Crystallography), lead to our seeking a suitable compound for an X-ray crystallographic study, and this was found from the reaction of Ti(*n*-BuO)$_4$ with diphenylsilandiol, $Ph_2Si(OH)_2$.

Reactions involving $Ph_2Si(OH)_2$

The work reported by Zeitler and Brown,[77] mentioned earlier, also included the reaction between tetra-*n*-butoxytitanium and diphenylsilanediol. They reported that different melting points were observed when the product was recrystallised from toluene or diethyl ether, *i.e.* 287–303 °C or 314–314.5 °C, respectively. This would appear to indicate that the product occurs in more than one polymorphic form. They postulated that the product recrystallised from diethyl ether was of the form $\overline{Ti[OSiPh_2(OSiPh_2)_3O]}_2$, '16-phenyloctasiloxyspiro(9.9)titanate' [later and more correctly referred to as hexadecaphenyloctasiloxyspiro(9,9)titanium].[41] A crystal structure analysis of the product crystallised from diethyl ether later confirmed the suggested molecular structure and was of particular interest because of the uncommon spiro-structure and unusual four-coordinate and tetrahedral geometry of Ti(IV).[41] Before realising that the crystal structure of this product had been reported,[41] we decided to investigate the apparent polymorphism reported by Zeitler and Brown.[77]

We carried out the reaction as reported by Zeitler and Brown,[77] reacting $Ph_2Si(OH)_2$ and Ti(*n*-BuO)$_4$ in diethyl ether under an inert atmosphere (see Eqn 15).

$$8\ Ph_2Si(OH)_2(s) + Ti(n\text{-}BuO)_4(l) \xrightarrow{Et_2O} \overline{Ti[OSiPh_2(OSiPh_2)_3O]}_2(s) + 4\ n\text{-}BuOH(l) + 6\ H_2O\ (l)$$

(Equation 15)

An immediate reaction was observed and the suspension of $Ph_2Si(OH)_2$ disappeared soon after the Ti(*n*-BuO)$_4$ was added. The solution was refluxed for 3 days, after which the solvent was evaporated under reduced pressure, leaving an orange-coloured oil. This was crystallised by adding hexane and scratching with a glass rod.

Some of the solid material was recrystallised from hot diethyl ether and yielded good quality crystals. The overall yield was calculated to be 11.2 %. The melting point was found to be 310–313 °C (lit.,[77] 314–314.5 °C), the C and H microanalyses were satisfactory and the ^{1}H NMR spectrum showed only the phenyl protons. The density was determined to be 1.176 (6) g cm^{-3} by flotation in a solution of potassium iodide in distilled water. A complete crystal structure analysis was performed, details of which can be found in Chapter 3 - X-Ray Crystallography. The molecular structure observed was as predicted by Zeitler and Brown[77] and showed the product to be hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) (see Figure 3).

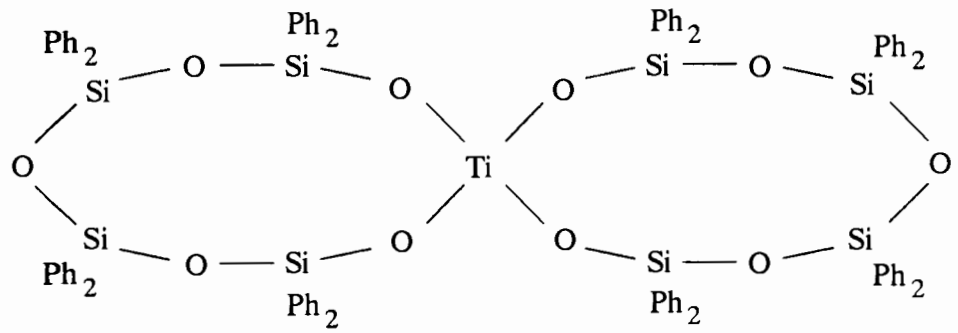


Figure 3 - The molecular structure of hexadecaphenyloctasiloxyspiro(9,9)titanium.

After the crystal structure had been solved, it was found that the structure had previously been determined by Hursthouse and Hossian.[41] The results of the work of this group are described and compared with the present structure in Chapter 3 – X-Ray Crystallography. Different reactants from those used here were used in the preparation of hexadecaphenyloctasiloxyspiro(9,9)titanium by Hursthouse and Hossian,[41] who reacted tetra-*iso*-propoxytitanium, $Ti[(CH_3)_2CHO]_4$, with diphenylsilanediol in diethyl ether. However, the molecular and crystal structures are identical.

Other cyclic metallasiloxane compounds similar to that described above have been reported in the literature:[40] $[Ti(OSiPh_2OSiPh_2O)_2]$ (6), *cis*-$\{Ti[OSiPh_2(OSiPh_2)_2O]_2(py)_2\}$ (8), $Li_2[Zr(OSiPh_2OSiPh_2O)_3].3py$ (13), and $(NEt_2H_2)_2[Zr(OSiPh_2OSiPh_2O)_3]$ (14). Some of these spirosiloxanes are discussed further in Chapter 3 – X-Ray Crystallography.

As mentioned earlier, Zeitler and Brown[77] reported different melting points when the product was recrystallised from diethyl ether or toluene. In an attempt to investigate the nature of the other crystalline form of the product, the crude product was recrystallised from a minimum of hot toluene (m.p. 314–315 °C). Preliminary X-ray photography revealed the same unit cell dimensions as found for the unit cell of the above crystal structure. This indicated, contrary to the results reported by Zeitler and Brown,[77] that the two solvents used for crystal growth yielded crystals with identical crystal structures.

Chapter Three

X-Ray Crystallography

CHAPTER 3
X-RAY CRYSTALLOGRAPHY

Crystallographic study of bis(cyclopentadienyl)bis(triphenylsiloxy)zirconium(II)

As was described earlier (refer to Chapter 2 – Results and Discussion) there were discrepancies between the literature melting point of $Cp_2Zr(OSiPh_3)_2$ (lit.,[42] m.p. 292–296 °C) and the melting point observed in the present study (*viz.* 187–190 °C). Even though the ^1H NMR, C and H microanalysis and XRF results indicated that $Cp_2Zr(OSiPh_3)_2$, had been found, it was thought that a crystal structure analysis would yield conclusive results and confirm the molecular structure beyond doubt.

Crystal and intensity data

Crystal preparation

Bis(cyclopentadienyl)bis(triphenylsiloxy)zirconium(II) was prepared and purified as described earlier (refer to Chapter 2 – Results and Discussion). Attempts were made to grow crystals by various methods, using different solvents and techniques. The method that yielded the best quality crystals involved dissolving some of the sample in a minimum of chloroform in a very small vial. This was placed in a desiccator containing a petri-dish filled with diethyl ether. The desiccator was sealed and then partially evacuated creating an ether atmosphere. An interface between the two solvents was effectively formed. After a few days very fine crystals were evident on the surface of the solution. After approximately a week, the crystals were large enough to use for X-ray crystallographic analysis. The crystals were separated from

the solvent system by pouring the contents of the vial onto filter paper and washing the solid crystalline material with hexane. Bis(cyclopentadienyl)bis(triphenylsiloxy)-zirconium(II) m. p. 184–187 °C. (Found: C, 71.3; H, 5.3 %. Calc. for $C_{46}H_{40}O_2Si_2Zr$: C, 71.5; H, 5.2 %).

Density determination

The density of the crystal was determined, in triplicate, by flotation in a solution of potassium iodide in distilled water. The density of the aqueous KI was measured with a Paar DMA 35 density meter and was found to be 1.282 (1) g cm^{-3} at 19.2 °C.

Preliminary X-ray analysis

A good quality crystal (1.0 x 0.7 x 0.3 mm) was selected and mounted on a Plasticine cone, which was pressed onto a goniometer head. By rotating the crystal in plane-polarised light, optical uniformity was detected *i.e.* no intergrown or twinned crystals were apparent. The crystal was optically aligned along the longest visible crystal edge by observing reflections from adjacent faces, using a Stoe 2-circle optical goniometer. The use of optical alignment proved to save time as alignment by photographic methods was not necessary.

Oscillation, Weissenberg, de Jong-Bouman, cone-axis and precession photographs were taken using either a Stoe-Weissenberg or a Reciprocal Lattice Explorer goniometer in conjunction with Philips PW 1120 and PW 1008 X-ray generators operating at 20 or 30 mA respectively and 40 kV. A copper target was used and Cu-K_α radiation (λ = 1.5418 Å) was obtained with the aid of a nickel filter. The X-ray films (Valca HPX-44) were processed by standard methods with Agfa-Gevaert X-ray developer and fixer solutions.

An oscillation photograph was taken revealing a mirror plane coincident with the zero layer-line. This indicated at least monoclinic symmetry, in which case the crystal was mounted along the *b*-axis. The corresponding cell dimension was found to be $b = 10.4$ Å using:

$$r = \frac{n\lambda}{\sin \tan^{-1} \frac{y_n}{R}}$$

(where $n = 1,2,3,...$

$\lambda = 1.5418$ Å

R = camera radius = 60 mm for Explorer and

y_n = the distance between corresponding rows on either side of the zero level).[78]

A de Jong-Bouman photograph of the *h0l* level of the reciprocal lattice was taken with a^* and c^* in the plane of the film. Only a two-fold axis was observed so the crystal system was monoclinic. β^* was found to be 82.27 ° (β = 97.73 °) by measuring the angle between the a^* and c^* axes. a was found to be 35.7 Å by:

$$a^* = \frac{x_n}{\lambda R}$$

(where x_n = the distance between rows of dots perpendicular to a^*

$\lambda = 1.5418$ Å,

R = camera radius = 60 mm

and $a = \frac{1}{a^* \sin \beta^*}$).[78]

Similarly c was found to be 21.1 Å.

The camera was set up for the *h1l* photograph and the following adjustments were necessary:-

the crystal was rotated clockwise by 25.38 ° so that c^* was vertical.

the angular setting μ_1 = 33.98 ° (where $\sin\mu_1 = \cos\psi_1 - \frac{\lambda}{b}$; ψ_1 = 45°, λ = 1.5418 Å and b = the measured cell length = 10.4 Å).[78]

the distance the film should be mounted from the zero level position, ν_1 = 8.86 mm (where $\nu_1 = \frac{\lambda M}{b}$; λ = 1.5418 Å, M = magnification factor = 60 mm and b = the measured cell length = 10.4 Å).

The photographs of the *h*0*l* and *h*1*l* levels were compared and there were systematic absences for l = 2n + 1 (n an integer), indicating a *c*-glide plane perpendicular to *b*.[78] Those reflections present in the *h*0*l* photograph had counterparts in the *h*1*l* photograph when the two levels were superimposed. This ruled out lattice centring. (For the monoclinic system, the latter would require that no two reflections from these levels should coincide).

A 30 ° precession photograph was taken using a 30 mm annulus, positioned 26 mm from the crystal, to view the 0*kl* plane. The value of b^* was calculated to be 0.09 $Å^{-1}$ as for a^* and c^* earlier. The value of *b* was found to be 10.42 Å (as $b = \frac{1}{b^*}$). The reflections observed along 0*k*0 were consistent with a two-fold screw axis parallel to *b* (*i.e.* absences for k = 2n + 1, for n an integer). The only exception was a strong (010) reflection which was possibly due to the Renninger effect.[78] Only reflections 0*k*0 with k_{max} = 6 were recorded, leaving the question of a two-fold screw axis parallel to *b* unresolved.

A precession photograph was also taken about *c* with a^* vertical to view the *hk*0 plane. Symmetry *mm* was observed as expected for a monoclinic crystal.

The space group was thus determined to be either *Pc*, *P*2/*c* or $P2_1/c$ (primitive, two-fold screw axis and a *c*-glide plane).[78]

Crystal data measured from X-ray photographs:

$a = 35.7$ Å	$b = 10.4$ Å	$c = 21.1$ Å
$\alpha = 90$ °	$\beta = 97.7$ °	$\gamma = 90$ °
$V = 7763$ Å	$Z = 8$	

If the space group is $P2_1/c$, then two molecules are required in the asymmetric unit as Z = 8.

Intensity data

The crystal used for the photography was cut to an appropriate size (0.35 x 0.35 x 0.30 mm) for the diffractometer data-collection and glued onto a glass fibre. A polaroid photograph was taken on the Reciprocal Lattice Explorer camera to observe the quality of the crystal being used for the intended data-collection. The spots on the film were clearly defined and the crystals appeared to diffract well.

All diffractometer work was performed using Mo-K_α radiation (λ = 0.71069 Å) on an Enraf-Nonius CAD4 diffractometer. During the preliminary stages the data indicated a triclinic cell and after many attempts to transform the base vectors found, it was not possible to obtain the monoclinic cell determined from the X-ray photography. The best triclinic cell found was as follows:

a = 35.7 Å	b = 10.4 Å	c = 21.1 Å
$\alpha = 90.4$ °	$\beta = 98$ °	$\gamma = 96$ °.

Three more crystals were mounted with similar results. A full data-collection was not initiated because of the failure of the diffractometer software to find the correct unit cell.

Crystal and Molecular structure of hexadecaphenyloctasiloxyspiro(9,9)titanium(IV)

Zeitler and Brown[77] proposed that the reaction between tetra-*n*-butoxytitanium and diphenylsilanediol should yield an interesting spiro-complex. Their results appeared to support this, but an X-ray crystallographic investigation seemed pertinent to confirm the suggested molecular structure.

Crystal and intensity data

Crystal preparation

Hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) was prepared and purified as described earlier (refer to Chapter 2 – Results and Discussion). The recrystallisation used to purify the product yielded crystals adequate for crystallographic studies. Hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) m.p. 310–313 °C. (Found: C, 69.2; H, 4.8. Calc for $C_{96}H_{80}O_{10}Si_8Ti$: C, 69.2; H, 4.8 %).

Density determination

The density of the crystal was determined in duplicate by the flotation method using an aqueous KI solution and was found to be 1.176 (6) g cm^{-3} at 22.3 °C.

Preliminary X-ray analysis

A good quality crystal was mounted and optically aligned as described earlier for bis(cyclopentadienyl)bis(triphenylsiloxy)zirconium(II). Similar camera settings, developing techniques and cell dimension calculations were used as those previously described.

An oscillation photograph displaying no symmetry indicated a cell dimension of 13.8 Å.

A 0-level de Jong-Bouman photograph revealed two mirror planes thus indicating a monoclinic crystal. The two axes were arbitrary labelled p^* and q^*, and p^* was found to be 0.0428 $Å^{-1}$ and q^* 0.0360 $Å^{-1}$. Polaroid photographs were taken to determine which of the two axes was b^*. When q^* was allowed to precess, a two-fold axis was observed whereas when p^* was allowed to precess, mirror symmetry was evident. This indicated that q^* was the symmetry axis b^*. Earlier q^* was found to be 0.0360 $Å^{-1}$ thus b^* was 0.0360 $Å^{-1}$ and b = 27.8 Å (as $b = \frac{1}{b^*}$).

A b cone-axis photograph was taken with the precession angle $\bar{\mu}$ = 10 ° to confirm the value of b. The true crystal to film distance (s) was found to be 29.92 mm:

$$s = \frac{r_0}{\tan\mu} \text{ where } r_0 = \text{the radius of the inner concentric circle.}^{79}$$

b was found to be 26.1 Å from $b = \frac{\lambda}{d^*}$ and $n\,d^* = \cos\bar{\mu} - \cos\tan^{-1}\frac{r_n}{s}$ (where λ = 1.5418 Å and r_n are the radii of the concentric circles for n = 1, 2, 3, 4, 5). The cell dimensions calculated from the de Jong-Bouman photographs are more accurate than those determined from the cone-axis photograph so b = 27.8 Å was considered to be the better estimate for b.

Photographs of the $h0l$ and $h1l$ levels were taken revealing absent rows in the 0-level. A convenient cell was selected and absences were observed for $h + l = 2n + 1$ (n an integer), indicating an n-glide plane perpendicular to b.[78] Cell dimensions were accurately determined from the $h0l$ and $h1l$ photographs as follows (refer to Figure 1):

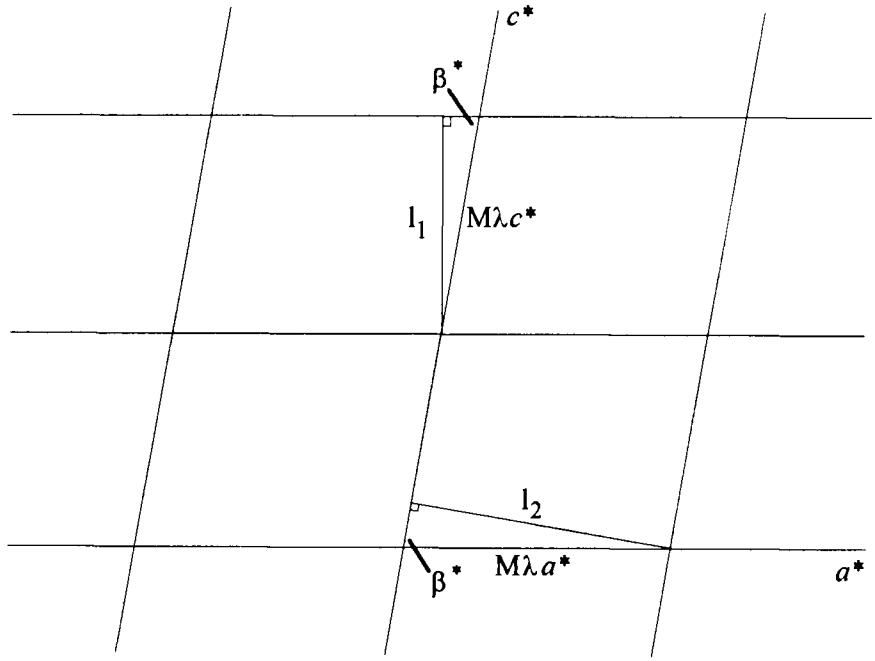


Figure 1

$a = \frac{M\lambda}{l_2}$ (from $l_2 = M\lambda a^* \sin\beta^*$ and $a = \frac{1}{a^* \sin\beta^*}$). Similarly for *c*. β* was found to be 85.6 ° (β = 94.4 °). Thus *a* and *c* were found to be 13.85 and 23.5 Å respectively.

A photograph of the *h*2*l* level was taken and was superimposable onto *h*1*l*, thus indicating that the lattice type was primitive. Inspection of the diffractometer intensity data subsequently collected also indicated systematic absences for 0*k*0, such that $k = 2n + 1$ (n an integer) thus indicating a two-fold screw axis parallel to *b*.[78] The intensity data also confirmed all the other conditions observed in the X-ray photography. The space group was thus uniquely determined to be $P2_1/n$. This is a non-standard setting but is listed in *International Tables for X-Ray Crystallography*.[80] The space group $P2_1/n$ is the same as $P2_1/c$ except for the

different choice of the *c*-axis. Figure 2 illustrates the relationship between the unit cells with space groups $P2_1/n$ and $P2_1/c$.

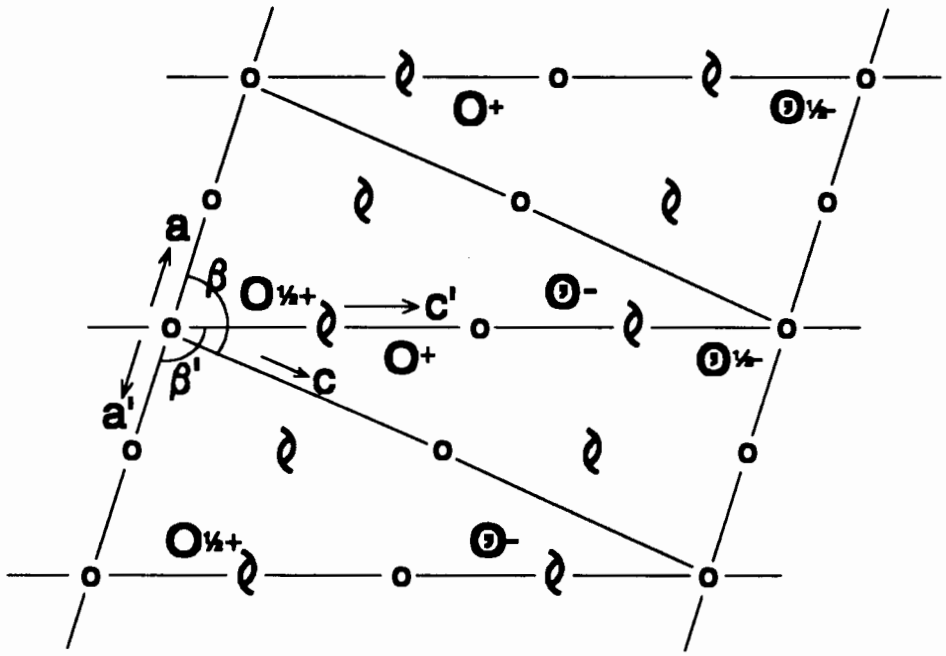


Figure 2 - The relationship between the unit cell (bounded by *a*, *b* and *c*) corresponding to the space group $P2_1/n$, and the unit cell (bounded by *a*', *b*' and *c*') corresponding to the space group $P2_1/c$. The equivalent positions are:

$P2_1/n$: *x*, *y*, *z*; -*x*, -*y*, -*z*; ½+*x*, ½-*y*, ½+*z*; ½-*x*, ½+*y*, ½-*z*

$P2_1/c$: *x*, *y*, *z*; -*x*, -*y*, -*z*; *x*, ½-*y*, ½+*z*; -*x*, ½+*y*, ½-*z*

The two cells are projected onto (010). Symmetry operation symbols are taken from Ref 80.

Intensity data

A good quality crystal was selected from the crystalline sample and cut to an appropriate size (0.25 x 0.25 x 0.20 mm) for the diffractometer data-collection. The

crystal was mounted onto a glass fibre and an oscillation photograph was taken to observe the quality of the crystal. The photograph indicated a good quality crystal as all the visible X-ray reflections were clearly defined.

The crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Graphite-monochromated MoK_α radiation (λ = 0.7107 Å) was used for the data-collection. Accurate unit cell dimensions were determined by least-squares analysis of the setting angles of 24 reflections in the range 16 ° ≤ θ ≤ 17 °. During the data-collection, three reference reflections were monitored every hour to check crystal stability. Orientation control was checked every 200 measured reflections. Data were corrected for Lorentz-polarisation effects and for absorption[81] using program EAC of the Enraf-Nonius Structure Determination Package.[82] Table 1 lists crystal data, and Table 2 the data-collection parameters.

Table 1 - Crystal Data for hexadecaphenyloctasiloxyspiro(9,9)titanium(IV)

Molecular formula	$C_{96}H_{80}O_{10}Si_8Ti$
Molecular mass (g mol^{-1})	1666.270
Space group	$P2_1/n$
a (Å)	13.805 (5)
b (Å)	27.545 (5)
c (Å)	23.476 (9)
α (°)	90
β (°)	94.41 (3)
γ (°)	90
Z	4
V (Å^3)	8901 (5)
D_c (g cm^{-3})	1.244

Table 1 - continued

D_m (g cm^{-3})	1.176 (6)
μ (Mo-K_α) (cm^{-1})	2.546
F(000)	3480

Table 2 - Data-collection parameters for hexadecaphenyloctasiloxyspiro(9,9) titanium(IV)

Crystal dimensions (mm)	0.25 x 0.25 x 0.20
Range scanned (°)	$1 \leq \theta \leq 25$
Range of indices	$-16 \leq h \leq 16$
	$0 \leq k \leq 32$
	$-27 \leq l \leq 0$
Reflections for lattice parameters: no., θ range (°)	24, $16 \leq \theta \leq 17$
Indices of standard reflections	-10 6 8, -6 4 16, -7 16 3
Average intensity variation for standard reflections (%)	+ 4.5
Scan mode	ω-2θ
Scan width in ω (°)	(0.80+0.35tanθ)
Vertical aperture length (mm)	4
Aperture width (mm)	(1.12+1.05tanθ)
Max. scan time (s)	40
Number of reflections collected	16432
Number of unique reflections	10865
R_{int}	0.0362
Number of reflections observed with $I_{rel} > 2\sigma (I_{rel})$	5528
Absorption corrections: min., max., average	0.9759, 0.9934, 0.9875

Solution and refinement of the structure

The data-collection confirmed the systematic absences observed in the X-ray photography and thus the space group $P2_1/n$. The first computations were performed using direct methods with the SHELX-86 computer program.[83] The atomic scattering factors for titanium were those of Ibers and Hamilton.[84]

A total of 512 normalised structure factors with $E_{min} \geq 1.20$ were involved in 5507 unique triple phase relationships. Fifty phase sets were refined and the program yielded the best solution with a combined figure of merit of 0.030. The E-map based on this phase set revealed the positions of 91 atoms of the molecule.

The skeleton of the spiro-structure was immediately evident as the positions of most of the non-hydrogen atoms had been determined, the only uncertainties being for some of the phenyl carbon atoms, which affected four rings. The molecular structure predicted by Zeitler and Brown[77] was thus confirmed.

The subsequent refinement of the structure was performed using the SHELX-76 program.[85] Initially, twelve of the sixteen phenyl rings were inserted into the model and constrained into rigid hexagons with the first atom acting as the pivot. After this run all of the non-hydrogen atoms were evident from the electron density map. These atoms were included with the original set of atoms and the phenyl rings were still constrained. The agreement between observed (F_o) and calculated (F_c) structure factors is expressed by the conventional residual index $R = \frac{\Sigma(||F_o| - |F_c||)}{\Sigma|F_o|}$. An R-value of 0.0957 was achieved after this stage, but 269 parameters were already being varied as the molecular structure was so large. The later refinement of the crystal structure was performed using the block-diagonal least-squares technique. This was because of the limitation of the version of software

being used which permitted a maximum of only 500 parameters to be used at any time. For the anisotropic refinement the thermal parameters were of the form T = $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ where U_{ij} are the anisotropic temperature factors expressed in terms of mean-square amplitudes of vibration in $Å^2$. The carbon atoms of the phenyl rings were no longer constrained and were allowed to vibrate isotropically. These steps resulted in a decrease to 0.0884 for the *R*-value. The largest unassigned peaks in the difference electron density map were only of the order characteristic of hydrogen atoms. The hydrogen atoms were all subjected to a constrained refinement, fixing the C-H bond length to 1.08 Å and their positions being dictated by the geometry of the molecule. The temperature factors of the hydrogens on the phenyl rings attached to the same silicons were linked to limit the number of parameters used. After this cycle the remaining electron density observed was insignificant indicating that all the atoms had been located. The structure factors were weighted according to wt α $\frac{1}{\sigma^2(F_o)}$. After eight refinement cycles, the final *R*-value was 0.0813 and R_w was 0.0697 where $R_w = \frac{\Sigma\, w^{1/2}||F_o| - |F_c||}{\Sigma\, w^{1/2}|F_o|}$. The analysis of variance (see Table 3) calculated after the final cycle showed the weighting scheme to be satisfactory. Table 4 lists the final refinement data.

Table 3 - Analysis of variance for hexadecaphenyloctasiloxyspiro(9,9)titanium(IV)

(a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	720	643	704	690	663	734	686	688	5528
V	492	459	478	463	470	514	470	475	478

(b) As a function of sin θ

sin θ	0.00 - 0.15	0.15 - 0.20	0.20 - 0.23	0.23 - 0.25	0.25 - 0.28	0.28 - 0.30	0.30 - 0.32	0.32 - 0.35	0.35 - 0.38	0.38 - 0.43
N	561	701	526	425	746	530	431	601	519	488
V	621	566	487	493	467	439	434	391	389	403

(c) As a function of $\sqrt{F/F_{max}}$

$\sqrt{F/F_{max}}$	0.00 - 0.23	0.23 - 0.25	0.25 - 0.27	0.27 - 0.28	0.28 - 0.30	0.30 - 0.32	0.32 - 0.35	0.35 - 0.38	0.38 - 0.44	0.44 - 1.00
N	637	618	725	309	609	529	593	438	519	551
V	407	372	419	439	474	477	533	566	505	585

(d) As a function of |Miller index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	315	620	575	566	547	482	457	425	370	320	273	205	147	97	129
V	584	557	522	497	456	442	456	446	430	409	440	474	400	419	400

$\|k\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	198	321	309	293	307	298	308	320	279	283	271	269	237	224	1611
V	646	524	491	454	466	537	501	479	463	468	500	492	489	454	431

$\|l\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	204	363	374	351	332	349	322	327	326	297	294	261	226	244	1258
V	576	523	517	474	486	519	494	513	459	456	503	497	434	469	416

N = No. of reflections in the group

$$V = 100\frac{M\Sigma(\omega|F_o - F_c|^2)}{N\Sigma\ \omega_i}$$

M = Total number of reflections.

Table 4 - Final refinement data for hexadecaphenyloctasiloxyspiro(9,9)titanium(IV)

Number of parameters	291
R	0.0831
R_w	0.0697
w	$\frac{2.7059}{\sigma^2(F_o)}$
S	3.4051
Max shift / e.s.d	0.026
Average shift / e.s.d	0.010
Max. height in difference Fourier map (e $Å^{-3}$)	0.502
Min. height in difference Fourier map (e $Å^{-3}$)	-0.536

The final atomic positional and thermal parameters can be seen in Table 1 (refer to Appendix), whilst Table 2 (refer to Appendix) lists the observed and calculated structure factors.

All computation work was carried out on the VMS-VAX at UCT using the following programs:

SHELX-86 [83] and SHELX-76 [85]	Data reduction, structure determination and refinement
PARST [86]	Bond distances, bond angles, torsion angles and least-squares planes
PLUTO-89 [87]	Molecular illustrations.

Description of the structure

Molecular structure and discussion

The molecule contains two ten-membered rings with a tetrahedrally bonded titanium atom as the junction. These rings are composed of alternate oxygen and silicon atoms with two phenyl rings connected to each silicon atom. Selected bond lengths and bond angles for hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) can be found in Tables 5 and 6 respectively. Complete lists of the bond lengths and bond angles are located in the Appendix (refer to Tables 3 and 4 respectively). Figure 3 illustrates the atomic nomenclature used and the molecular structure. Figure 4 shows an unlabelled stereoscopic view of the molecular structure and the conformation of the two titanosiloxane rings bonded to the central titanium atom can clearly be seen.

Table 5 - Selected bond lengths (Å) with estimated standard deviations in parentheses for the least significant figure for hexadecaphenyloctasiloxy-spiro(9,9)titanium(IV).

Ti(1)	-	O(1)	1.793(5)	Si(4)	-	O(4)	1.608(6)
Ti(1)	-	O(5)	1.780(6)	Si(4)	-	O(5)	1.628(6)
Ti(1)	-	O(6)	1.777(6)	Si(5)	-	O(6)	1.629(6)
Ti(1)	-	O(10)	1.788(7)	Si(5)	-	O(7)	1.613(6)
				Si(6)	-	O(7)	1.611(6)
Si(1)	-	O(1)	1.628(6)	Si(6)	-	O(8)	1.620(7)
Si(1)	-	O(2)	1.613(6)	Si(7)	-	O(8)	1.61(6)
Si(2)	-	O(2)	1.611(6)	Si(7)	-	O(9)	1.620(7)
Si(2)	-	O(3)	1.608(7)	Si(8)	-	O(9)	1.608(6)
Si(3)	-	O(3)	1.607(7)	Si(8)	-	O(10)	1.614(7)
Si(3)	-	O(4)	1.616(7)				

Table 5 -continued.

Si(1)	-	C(1)	1.852(9)	Si(5)	-	C(49)	1.84(1)
Si(1)	-	C(7)	1.84(1)	Si(5)	-	C(55)	1.85(1)
Si(2)	-	C(13)	1.86(1)	Si(6)	-	C(61)	1.87(1)
Si(2)	-	C(19)	1.837(9)	Si(6)	-	C(67)	1.83(1)
Si(3)	-	C(25)	1.86(1)	Si(7)	-	C(73)	1.854(9)
Si(3)	-	C(31)	1.85(1)	Si(7)	-	C(79)	1.858(9)
Si(4)	-	C(37)	1.853(9)	Si(8)	-	C(85)	1.853(9)
Si(4)	-	C(43)	1.84(1)	Si(8)	-	C(91)	1.835(9)

All	C	-	C	1.31(1)	- 1.47(1)

Table 6 - Selected bond angles (degrees) with estimated standard deviations in parentheses for the least significant figure for hexadecaphenyloctasiloxy-spiro(9,9)titanium(IV).

O(6)	-	Ti(1)	-	O(10)	107.7(3)	Si(1)	-	O(2)	-	Si(2)	147.6(4)
O(5)	-	Ti(1)	-	O(10)	108.9(3)	Si(2)	-	O(3)	-	Si(3)	157.8(5)
O(5)	-	Ti(1)	-	O(6)	109.4(3)	Si(3)	-	O(4)	-	Si(4)	150.1(5)
O(1)	-	Ti(1)	-	O(10)	109.7(3)	Si(5)	-	O(7)	-	Si(6)	172.0(5)
O(1)	-	Ti(1)	-	O(6)	110.7(3)	Si(6)	-	O(8)	-	Si(7)	161.2(5)
O(1)	-	Ti(1)	-	O(5)	110.5(3)	Si(7)	-	O(9)	-	Si(8)	145.0(5)
Ti(1)	-	O(1)	-	Si(1)	162.1(4)	Ti(1)	-	O(6)	-	Si(5)	156.6(4)
Ti(1)	-	O(5)	-	Si(4)	174.2(4)	Ti(1)	-	O(10)	-	Si(8)	172.5(5)

Table 6 -continued.

O	-	Si	-	O	107.3(4) - 110.6(4)
C	-	Si	-	C	110.9(4) - 114.4(4)
O	-	Si	-	C	105.4(4) - 112.0(4)
C	-	C	-	C	114(1) - 131(1)

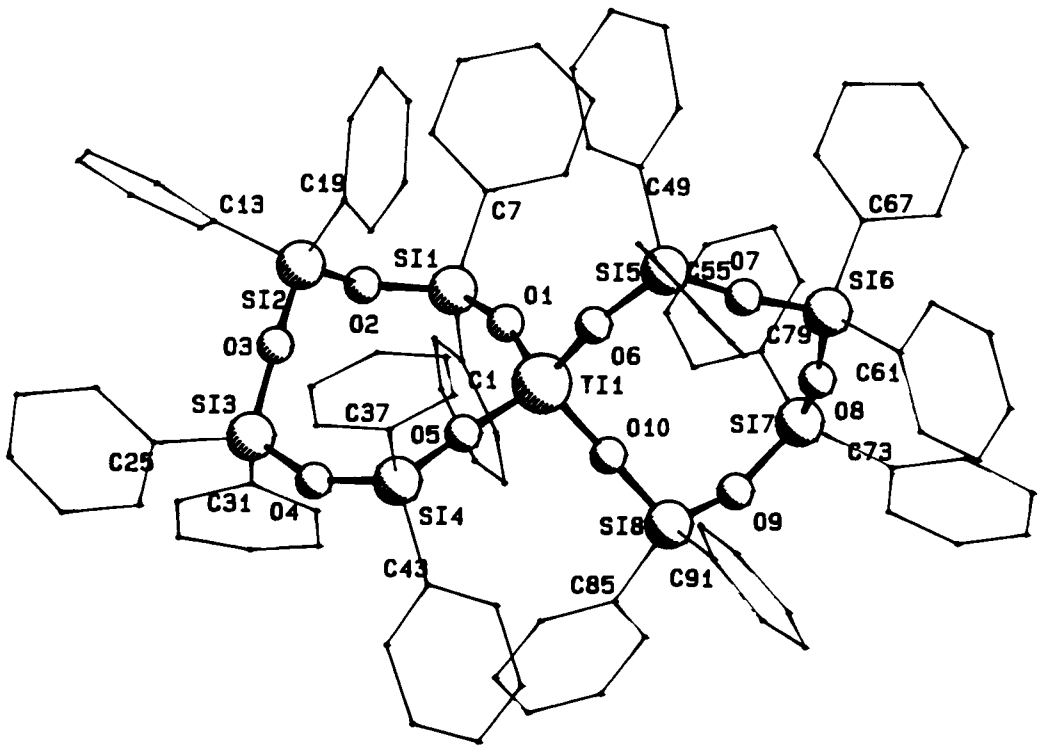


Figure 3 - PLUTO drawing representing the molecular structure of hexadecaphenyl-octasiloxyspiro(9,9)titanium(IV) showing the nomenclature. The hydrogen atoms, which have been omitted, are numbered according to the atom to which they are bonded.

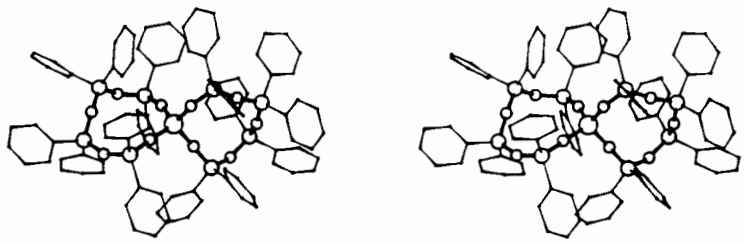


Figure 4 - A stereoscopic view of hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) showing the molecular structure and particularly the conformation of the titanosiloxane rings.

When the crystal structure of this compound was determined, it was not known that the structure had previously been published by Hursthouse and Hossian.[41] A comparison of the two structural studies follows in Table 7 overleaf.

The cell dimensions probably do not differ significantly. The difference could be attributed to data-collections being performed at different temperatures. This can not be established as the temperature of the data-collection by Hursthouse and Hossian[41] was not reported. Both the reported and our method of refinement involved a similar technique of blocking portions of the molecule during the refinement. This is inclined to yield results with unrealistically small estimated standard deviations. The bond distances and angles thus show satisfactory agreement. Hursthouse and Hossian[41] used 10652 observed data whereas we used 5528, but this did not result in dramatically improved results. The R and R_w values were also comparable.

Table 7 - Comparison of results between Hursthouse and Hossian[41] and the present study.

		Present study	Hursthouse and Hossian[41]
Crystal size (mm)		0.25 x 0.25 x 0.20	0.45 x 0.13 x 0.10
X-ray radiation		Mo-K_α	Cu-K_α
Cell dimensions [a (Å), b (Å), c (Å), β (°)]		13.805 (5) 27.545 (5) 23.476 (9) 94.41 (3)	13.829 (1) 27.594 (2) 23.514 (2) 94.39 (1)
Temperature at which data were collected (°C)		23	–
Number of observed reflections		5528 using $F_o>4\sigma F_o$	10652 using $F_o>3\sigma F_o$
Hydrogens included in refinement		Y	N
Bond distances (Å)	Ti–O	1.777(6)–1.793(5)	1.777(5)–1.791(5)
	Si–O	1.608(6)–1.629(6)	1.608(5)–1.635(5)
	Si–C	1.83(1)–1.87(1)	1.850(6)–1.868(6)
Bond angles (°)	O–Ti–O	107.7(3)–110.7(3)	107.9(2)–110.0(2)
	O–Si–O	107.3(4)–110.6(4)	107.3(2)–110.6(2)
	C–Si–C	110.9(4)–114.4(4)	110.3(3)–114.6(3)
	Si–O–Ti	156.6(4)–174.2(4)	156.4–173.3
	Si–O–Si	145.0(5)–172.0(5)	143.8–172.5

The central titanium atom is bonded to the four adjacent oxygen atoms in a tetrahedral geometry as indicated by the O-Ti-O angle range of 107.7–110.7(3) °. The dihedral angle between the planes of the O_2Ti segments of the titanosiloxane rings was calculated (program PARST) to be 89.8 (2) °, which is consistent with the

tetrahedral geometry of the titanium atom. Four-coordinate Ti(IV), especially with tetrahedral geometry is rare, disregarding the psuedo-tetrahedral structures of dicyclopentadienyl Ti(IV) derivatives. Some other examples of tetrahedral Ti(IV) are $\overline{Ti(NMeSiMe_2SiMe_2MeN)_2}$,[88] $\overline{Ti(NBu^tSiMe_2Bu^tN)_2}$,[89] $\overline{Ti(OSiPh_2OSiPh_2O)_2}$,[90] $TiCl[N(SiMe_3)_2]_3$,[91] μ-oxobis(tribenzyltitanium),[92,93] tetrabenzyl titanium[94] and dibenzylbis(octamethyl-2,4,6-trisila-1,3,5-triazacyclohex-1-yl)titanium.[95] The first three are also spiro molecules.

The eight silicon atoms also possess near tetrahedral geometry as O-Si-O bond angles of 107.3–110.6 (4) °, O-Si-C bond angles of 105.4 - 112.0 (4) ° and C-Si-C bond angles of 110.9–114.4 (4) ° were found. The C-Si-C bond angles are slightly larger than the ideal tetrahedral angle of 109.5 ° which is possibly due to steric hinderance of the bulky phenyl groups bonded directly to the silicon atoms. The dihedral angles between the planes defined by O-Si-O and C-Si-C units are between 87.5 (3) and 92.5 (4) °, substantiating the tetrahedral character of the silicon atoms' coordination. A table of dihedral angles around the titanium and silicon atoms (*i.e.* the angle between the planes defined by the atoms adjacent to the silicon and titanium atoms) can be found in the Appendix, Table 5.

The Si-O-Si bond angles differ significantly from 110 °, as predicted by the VSEPR model, *i.e.* between 145.0 and 172.0 (5) ° (refer to Table 6). Figure 5 shows a schematic representation of the $Ti(O_4Si_5)_2$ ring conformation. The values inside the rings indicate the Si-O-Si bond angles and the atomic deviations (Å x 10^2) from the least-squares planes are outside the rings. These deviations are discussed later. Large Si-O-Si bond angles as observed here have been reported previously, some of which are listed in Table 8. Cruickshank[96] discussed the geometry adopted by the Si-O-Si bridges in terms of Si-O π-bonding, concluding that high π-bond order is associated with an opening of the Si-O-Si bond angle. If this is applied to the

Ti-O-Si bond angles, which are between 156.6 (4) and 174.2 (4) °, high π-bond order is predicted. This would account for the relatively small Ti-O bond distances described later (*i.e.* large bond order).

Table 8 - A list of previously reported molecular structures with large Si-O-Si bond angles.

Author (s)	Molecule	Si-O-Si angle (°)
Almenningen *et al.*[97]	$O(SiH_3)_2$	144.1
Airey *et al.*[98]	$O(SiF_3)_2$	155.7
Airey *et al.*[99]	$O(SiCl_3)_2$	146
Barrow *et al.*[100]	$O(SiMe_3)_2$	148.8
Glidewell *et al.*[28]	$O(SiPh_3)_2$	176.8
Hossian and Hursthouse[31]	$[Ph_2Si(OH)]_2O$	147.8, 157.0 and 162.5
Suwinska *et al.*[29]	$(Ph_3Si)_2O.½C_6H_6$	180.0
	$(Ph_3Si)_2O.½C_5H_{11}N$	180.0
Wojnowski *et al.*[101]	$(HPh_2Si)_2O$	160
Voronkov *et al.*[102]	$Ph_3SiOSiPh_2Me$	158.9
Wojnowski *et al.*[103]	$[(t\text{-}BuO)_3Si]_2O$	144.0
Karle *et al.*[104]	$(t\text{-}BuPh_2Si)_2O$	152.4
Wiberg *et al.*[30]	$(t\text{-}Bu_3SiNHSiBu^t_2)_2O$	180
Wiberg *et al.*[30]	$(t\text{-}Bu_3Si)_2O$	179.1

Table 8 - continued

Hossian *et al.*[40]	*cis*-[Ti{OSiPh$_2$(OSiPh$_2$)$_2$O}$_2$-(py)$_2$].2C$_6$H$_5$Me	146.4 and 156.0
	Li$_2${Zr(OSiPh$_2$OSiPh$_2$O)$_3$}.3py.1.5-C$_6$H$_5$Me	132.2, 133.4 and 131.1
Feher[47]	Cp*Zr{(Si$_7$O$_{12}$)(*c*-C$_6$H$_{11}$)$_7$}	151 and 151
Feher *et al.*[49]	Cy$_7$Si$_7$O$_9$(OH)$_3$	145.5–161.1
	Cy$_8$Si$_8$O$_{11}$(OSnPh$_3$)$_2$	145.5–161.3

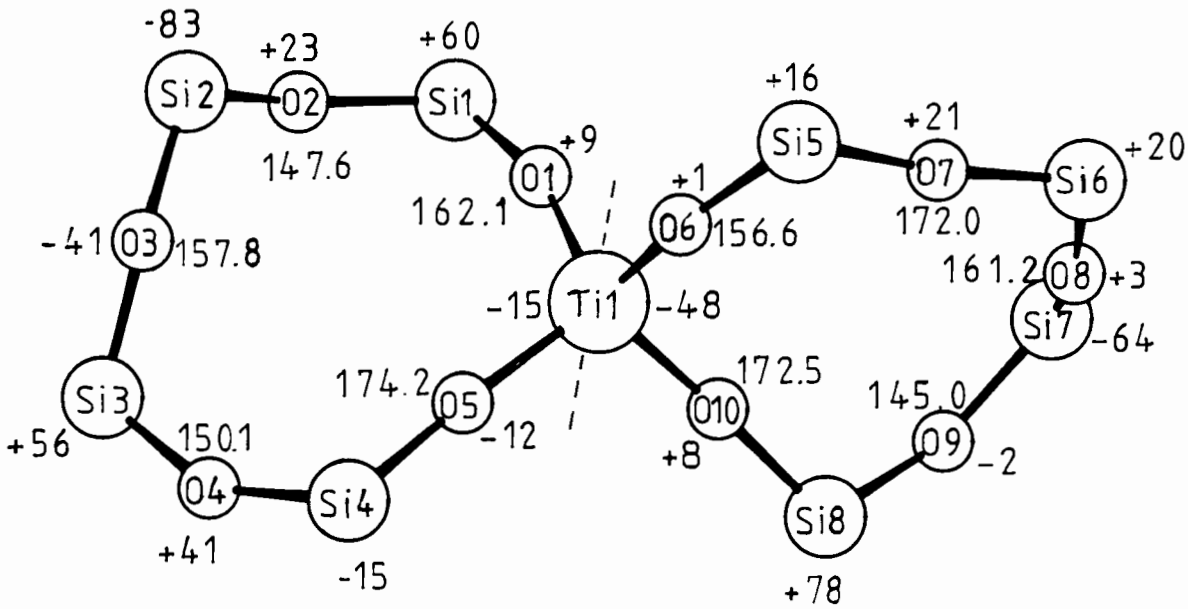


Figure 5 - A schematic representation of Ti(O$_4$Si$_5$)$_2$, with Si-O-Si and Ti-O-Si bond angles given inside the ring and the atomic deviations (Å x 10^2) from the least-squares plane on the outside.

The Ti-O bond lengths range between 1.777 (5) and 1.793 (5) Å (refer to Table 5) compared to the literature values for Ti-O of 1.820 (0.028) Å for μ-O,[105] 1.847 (0.055) Å for O-C (sp^3),[105] 1.873 (0.064) Å for O-C$_{ar}$,[105] 1.804 (7) Å for μ-oxobis(tribenzyltitanium),[93] 1.808 (7) Å for βBa$_2$TiO$_4$[106] and 1.73–1.87 Å for

Rb_2TiO_3.[107] The observed Ti-O bond lengths indicate very strong bonds and appear to be slightly stronger than most of those in the literature, as discussed earlier. The Si-O bond lengths, 1.608–1.629 (6) Å, agree well with the literature values of 1.622 (0.014) Å.[108] Similarly, the Si-C bond lengths, 1.83–1.87 (1) Å, show very little deviation from the expected literature values of 1.868 (0.014) Å.[108] A fairly wide range was observed for the C-C(phenyl) bond lengths, 1.31–1.47 (1) Å, with only a few deviating significantly from the literature range of 1.380 (0.013) Å.[108]

Least-squares planes were calculated for all the rings in the molecule (*i.e.* the titanosiloxane and phenyl rings) using the PARST computer program.[86] As would be expected, the two titanosiloxane rings clearly deviate significantly from planarity and the atomic deviations from the least-squares planes (Å x 10^2) are shown in Figure 5. Figures 6 and 7 clearly illustrate the deviations with two different views of the molecule. Figure 6 views the molecule almost parallel to the Ti(1)-O(1)-Si(1)-O(2)-Si(2)-O(3)-Si(3)-O(4)-Si(4)-O(5) ring, whereas Figure 7 views almost parallel to the Ti(1)-O(6)-Si(5)-O(7)-Si(6)-O(8)-Si(7)-O(9)-Si(8)-O(10) ring.

Both rings are irregular and can best be described by the torsion angles, which are listed in Table 9. A complete list of torsion angles can be found in Appendix, Table 6. Comparison of the two sets of angles seems to indicate that the conformation of the two rings is not related and that their conformation is presumeably dictated by the attached phenyl groups, which orientate themselves in such a way as to minimise steric hinderance.

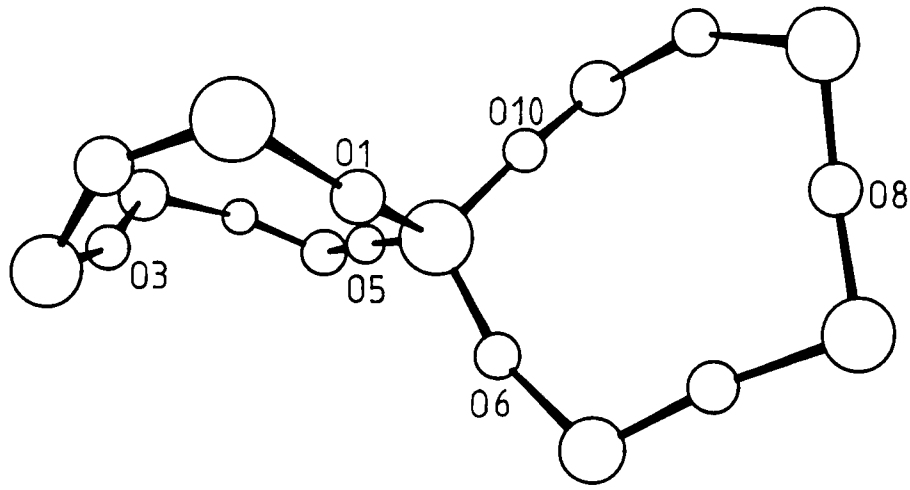


Figure 6 - View of hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) almost parallel to the Ti(1)-O(1)-Si(1)-O(2)-Si(2)-O(3)-Si(3)-O(4)-Si(4)-O(5) ring illustrating its conformation.

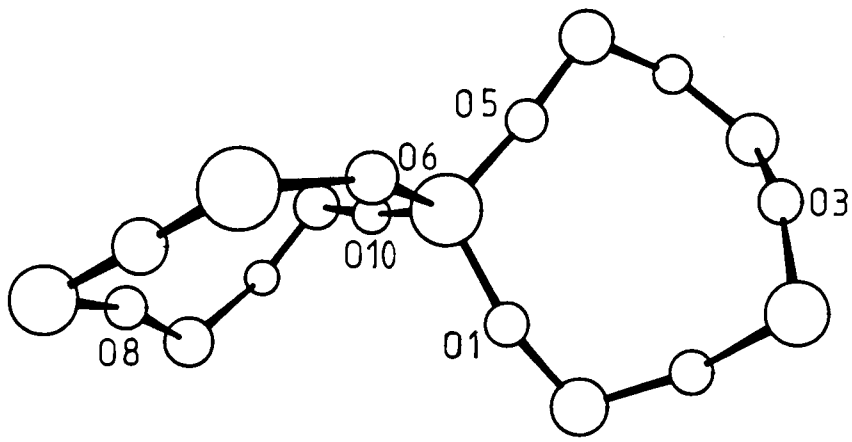


Figure 7 - View of hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) almost parallel to the Ti(1)-O(6)-Si(5)-O(7)-Si(6)-O(8)-Si(7)-O(9)-Si(8)-O(10) ring illustrating its conformation.

Table 9 - Selected torsion angles (degrees) with estimated standard deviations in parentheses for the least significant figure for hexadecaphenyloctasiloxy-spiro(9,9)titanium(IV).

O(5)-Ti(1)-O(1)-Si(1)	-33(1)		O(10)-Ti(1)-O(6)-Si(5)	51(1)
Ti(1)-O(1)-Si(1)-O(2)	56(1)		Ti(1)-O(6)-Si(5)-O(7)	-29(1)
O(1)-Si(1)-O(2)-Si(2)	37.9(1)		O(6)-Si(5)-O(7)-Si(6)	162(2)
Si(1)-O(2)-Si(2)-O(3)	-96.6(9)		Si(5)-O(7)-Si(6)-O(8)	-160(2)
O(2)-Si(2)-O(3)-Si(3)	-40(1)		O(7)-Si(6)-O(8)-Si(7)	87(1)
Si(2)-O(3)-Si(3)-O(4)	120(1)		Si(6)-O(8)-Si(7)-O(9)	-126(1)
O(3)-Si(3)-O(4)-Si(4)	-11(1)		O(8)-Si(7)-O(9)-Si(8)	19.0(9)
Si(3)-O(4)-Si(4)-O(5)	-35(1)		Si(7)-O(9)-Si(8)-O(10)	50.0(9)
O(4)-Si(4)-O(5)-Ti(1)	-177(3)		O(9)-Si(8)-O(10)-Ti(1)	-137(2)
Si(4)-O(5)-Ti(1)-O(1)	-169(3)		Si(8)-O(10)-Ti(1)-O(6)	64(2)

As expected, all the phenyl rings are planar with the greatest deviation from planarity being atom C(34) which deviates from the calculated least-squares plane by 0.10 (0.02) Å. This was considered satisfactory.

Molecular packing

As mentioned earlier, there are four molecules in the unit cell. These can be seen in Figure 8, which shows a stereoscopic view of the unit cell constants.

The PARST output indicated 530 intermolecular contacts less than 3.5 Å and these were all due to C···H and H···H interactions. The smallest of such interactions is 2.24(2) Å for the H(90)···H(58) intermolecular contact. None of these are considered to be significant. Figure 9 shows a stereoscopic view down the *a*-axis of the unit cell expanded along the *b*- and *c*-directions. The phenyl carbons have been

omitted from the plot for clarity. The pivot atom of the phenyl ring, however, has been included and can be seen attached to the basic spirosiloxane ring structures.

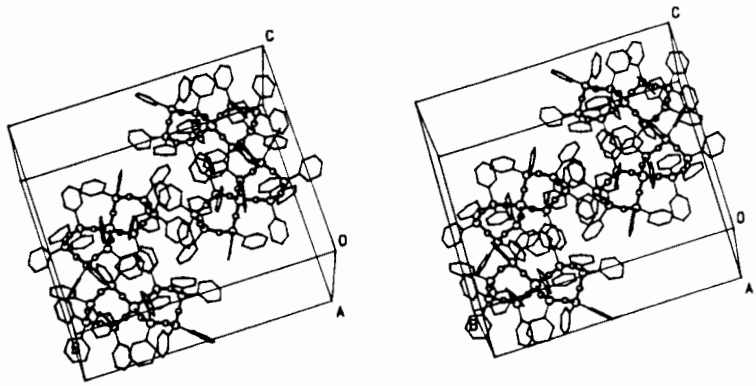


Figure 8 - A stereoscopic view of the crystal structure of hexadecaphenyloctasiloxy-spiro(9,9)titanium(IV).

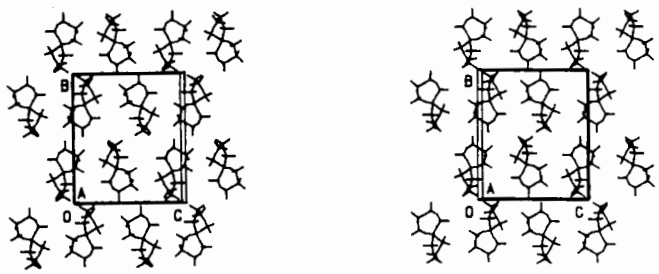


Figure 9 - A stereoscopic view down the *a*-axis illustrating the molecular packing in the *b*- and *c*-directions.

Discussion

Structures of other spiro-type molecules have been reported in the literature. Examples of metallasilazanes are $\overline{Ti(NMeSiMe_2SiMe_2MeN)}_2$,[88] $(C_6H_5CH_2)_2\overline{Ti[N(SiMe_2NMe)_2SiMe_2]}_2$ [95] and $\overline{M[(NBu^t)_2SiMe_2]}_2$ (M = Ti or Zr).[89] Of particular interest are the cyclic metallasiloxanes, examples of which include *cis*-$\{\overline{Ti[OSiPh_2(OSiPh_2)_2O]}_2(py)_2\}$, 8,[40] $Li_2[\overline{Zr(OSiPh_2OSiPh_2O)}_3.3py$, 13,[40] $(NEt_2H_2)_2[\overline{M(OSiPh_2OSiPh_2O)}_3]$, (M = Zr, Hf), 14, 15[31] and $\overline{Ti(OSiPh_2OSiPh_2O)}_2$, 6.[90]

Pyridine was added to concentrated solutions of the products of the reaction between MCl_4 (M = Ti or Zr) and $Si_2Ph_4O(OLi)_2$ to yield compounds 8 and 13.[40] Compound 6 was prepared by the reaction of $TiCl_4$ with $Si_2Ph_4O(OH)_2$.[90] When 6 was treated with a toluene-pyridine mixture, a ring expansion occurred with the formation of 8. Hossain *et al.*[40] proposed that the apparently facile formation of the cyclic titanatrisiloxane 8 is promoted by ring strain in the cyclic titanadisiloxane system, 6. This suggests that silane ring expansion, as observed by our present study, occurred in order to relieve the ring strain and not because the precursor disiloxanediolate was intrinsically unstable in the presence of base or metal halide compounds.[40]

Chapter Four

Experimental

CHAPTER 4
EXPERIMENTAL

General

All reagents were analytically pure and mostly supplied by Aldrich. The solvents used in the preparative work were all analytical grade and were pre-dried by various established methods. All preparative reactions were carried out under an inert atmosphere of pre-dried nitrogen. Microanalyses were performed by Mr P. Benincasa, on a Heraeus Universal Combustion Analyser, Model CHN-Rapid, at the Department of Chemistry, University of Cape Town or by Mrs M. Maska, on a Carlo-Erba Model 1106, at the Department of Energy Technology, CSIR, Pretoria. Melting points were measured on a Linkam hot stage with a Nikon SM2-10 microscope or a Reichert-Jung Thermovan. Proton NMR spectra were recorded on a Varian VXR200 spectrophotometer at 200 MHz using TMS (0.0 ppm) as an internal standard, by Ms M. M. Nair and Mr N. W. Hendricks, Department of Chemistry, University of Cape Town. X-Ray fluorescence analyses were carried out at the Department of Geochemistry, University of Cape Town. Mass spectrometry analyses were performed by Mr P. Boschoff, Cape Technikon, Cape Town.

Reactions involving tri-*n*-butylsilanol (*n*-Bu_3SiOH)

Preparation of n-Bu_3SiOH

*(a) from tri-*n*-butylsilane (*n*-Bu_3SiH) and silver nitrate*

Neat *n*-Bu_3SiH (14.0 cm^3, 10.9 g, 54.0 mmol, lit.,[62] b.p. 225–6 °C at 760 mmHg) was added to powdered $AgNO_3$ (19.924 g, 117 mmol) under nitrogen. The reaction commenced immediately, with NO_2 being evolved as a brown gas; the mixture initially changed to a darker colour, but became light grey as the NO_2 was expelled. The system was then heated to 140 °C and maintained at this temperature for 48 hours to drive the reaction to completion. The system was cooled when the reaction had visibly ceased. The crude oily product was dissolved in hexane and the metallic silver was removed by filtration. The hexane was removed under reduced pressure leaving a viscous, yellow-coloured oil. The yield of the crude product was 9.20 g. The yield of the silver deposit was 17.63 g.

The *n*-Bu_3SiOH was separated from the crude product by a controlled Kugelrohr vacuum distillation, giving two distinct fractions (the first few drops of the distillate were discarded):

i) 90 °C, 2.0 mmHg (lit.,[25] b.p. 140–1 °C at 760 mmHg), (6.59 g, 56.0 %), (Found: C, 65.0; H, 11.3. Calc. for $C_{12}H_{28}OSi$: C, 66.6; H, 13.0 %); $\delta_H(CDCl_3)$ 0.57 (6 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.81 (9 H, t, *J* 6.85, $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.31 (12 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.60 (1 H, br. s, *n*-Bu_3SiOH).

ii) >130 °C, 2.0 mmHg (lit.,[25] b.p. 190–200 °C at 760 mmHg), (2.05 g), (Found: C, 64.4; H, 11.6. Calc. for $C_{24}H_{54}OSi_2$: C, 66.9; H, 12.65 %); $\delta_H(CDCl_3)$ 0.52 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$), 0.88 (9 H, t, *J* 6.67, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$) and 1.30 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$).

*(b) from chlorotri-*n*-butylsilane (*n*-Bu_3SiCl) and potassium hydroxide*

KOH (3.11 g, 55.5 mmol) was dissolved in ethanol (*ca.* 80 cm^3). *n*-Bu_3SiCl (10.2 cm^3, 8.09 g, 32 mmol, lit.,[62] b.p. 124–5 °C) was added whereupon a fine, white precipitate formed immediately. The mixture was heated at reflux for 48 hours, after which time a slightly pink colour could be discerned. The ethanol was then evaporated under reduced pressure and the crude product separated from the white precipitate (KCl) by extraction into hexane (3 × 30 cm^3). The yield of the KCl was 2.47 g. The hexane was evaporated from the solution leaving a viscous oil (7.63 g).

The *n*-Bu_3SiOH was separated from the crude product by a controlled Kugelrohr vacuum distillation, giving two distinct fractions (the first few drops of the distillate were discarded):

i) 90 °C, 1.0 mmHg (6.33 g, 84.9 %), (Found: C, 66.9; H, 12.4. Calc. for $C_{12}H_{28}OSi$: C, 66.6; H, 13.0 %); $\delta_H(CDCl_3)$ 0.58 (6 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.87 (9 H, t, *J* 6.76, $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.16 (3 H, t, *J* 6.97, CH_3CH_2OH), 1.32 (12 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.50 (1 H, br. s, $[CH_3(CH_2)_2CH_2]_3SiOH$) and 3.66 (2 H, q, *J* 6.97, CH_3CH_2OH).

ii) > 130 °C, 1.0 mmHg, (0.36 g); $\delta_H(CDCl_3)$ 0.49 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$), 0.88 (9 H, t, *J* 6.67, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$) and 1.29 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$).

Reaction between tri-*n*-butylsilanol (*n*-Bu_3SiOH) and sodium hydride

A slurry of NaH (1.25 g, 80 % dispersion in mineral oil, 42 mmol) in dry THF (*ca.* 60 cm^3) was prepared and cooled to -78 °C using a dry-ice and acetone bath. *n*-Bu_3SiOH (6.00 g, 27.7 mmol) was dissolved in diethyl ether and added to the cooled mixture. No reaction was apparent before the system was allowed to warm to

room temperature. After one hour at room temperature the mixture became lighter and a white precipitate was evident around the edges of the flask. The mixture was allowed to stir for a further 21 hours after which a yellow solution and excess NaH was evident. The solution was decanted to separate the crude product from the NaH, which was washed with THF (2 × 5 cm^3), which was then added to the decanted solution. The unreacted NaH was neutralised with *iso*-butanol.

The solvent was removed under reduced pressure and the remaining oil cooled to 0 °C without crystallisation. Crystallisation from petroleum ether, diethyl ether and THF in separate experiments proved unsuccessful, even when the solutions were cooled to -78 °C. After the solution had been left to stand open overnight to allow evaporation, a gel-like substance resulted, with no evidence of crystallisation. This was washed with hexane and filtered off despite not being properly crystalline. Attempted cystallisation by dissolving the sample in a mixture of hot distilled water and ethanol proved successful; the solution was allowed to cool and, with scratching, sticky white crystals were formed. The mixture was cooled to 0 °C and the crystals filtered off and washed with cold ethanol.

The crystals were dried in a desiccator overnight yielding better quality crystals (0.92 g), m.p. > 350 °C (Found: C, 11.1; H, 2.0. Calc. for $Na^+\{OSi[(CH_2)_3CH_3]_3\}^-$: C, 60.4; H, 11.4 %); $\delta_H(D_2O)$ 1.04 (3 H, t, *J* 7.0, $CH_3CH_2O^-$) and 3.50 (2 H, q, *J* 7.1, $CH_3CH_2O^-$).

Reaction between* n-*Bu_3SiOH* *and* n-*butyllithium

n-Bu_3SiOH (1.00 g, 4.63 mmol) was dissolved in dry hexane (*ca.* 10 cm^3) and the temperature of the system was lowered to -78 °C. *n*-BuLi (3.0 cm^3, 1.6 M in

hexane, 4.8 mmol) was added, *via* a rubber septum, and the system was allowed to stir for 24 hours coming gradually to room temperature. The solution was cooled to -78 °C to promote crystallisation, but no precipitate was observed. The solvent was evaporated and a wet powder remained. This product was dried in a desiccator overnight with no change in appearance *i.e.* it still appeared wet. The solid was washed with hexane to remove any oil and filtered from the solvent to leave a white solid (0.07 g) (Found: C, 39.0; H, 9.4. Calc. for $Li^{+}\{OSi[(CH_2)_3CH_3]_3\}^{-}$: C, 64.8; H, 6.8 %); $\delta_H(CDCl_3)$ 0.58 (6 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.88 (9 H, t, *J* 6.73, $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.32 (12 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.82 (1 H, br. s, *n*-Bu_3SiOH).

Reaction between n-Bu_3SiOH and tantalum pentachloride

(a) without the use of a base

$TaCl_5$ (0.97 g, 2.7 mmol) was added to neat *n*-Bu_3SiOH (3.49 g, 16 mmol) with no visible reaction. The mixture was stirred for two hours without progress so the system was heated to 135 °C and was allowed to reflux for 3 days; again no reaction was observed. The system was allowed to cool and the deposit filtered off, washed with hexane and dried in a desiccator. Various analyses were performed on the white solid (0.79 g), m.p. > 350°C (Found: C, 0; H, 0 %). The white powder was heated in a crucible: it became brown, then white again and remained this colour even with intense heating.

The hexane was evaporated from the filtrate leaving a viscous, yellow oil (2.87 g), (Found: C, 67.7; H, 11.7. Calc. for $C_{24}H_{56}OSi_2$: C, 69.1; H, 13.5 %); $\delta_H(CDCl_3)$ 0.49 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.87 (9 H,

m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.29 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.53 (0.1 H, s, trace of *n*-Bu_3SiOH).

(b) with the use of the base, triethylamine

$TaCl_5$ (0.61 g, 1.70 mmol) was placed in a round-bottomed flask and the system was sealed. Addition of the solvent benzene (*ca.* 15 cm^3) *via* a rubber septum immediately followed by *n*-Bu_3SiOH (0.73 g, 3.4 mmol) gave no visible reaction. The base, triethylamine (0.5 cm^3, 0.36 g, 3.6 mmol), was added and an immediate reaction was observed as a white gas was formed and gradually disappeared. Reaction was stopped after three hours and the precipitate filtered off and washed with cold benzene to give a white solid (0.87 g), m.p. 196–199 °C sublim., but some remained < 600 °C (Found: C, 19.0; H, 5.7; N, 3.5. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.40 (9 H, t, *J* 7.33, $(CH_3CH_2)_3NH^+Cl^-$), 1.65 (1.3 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.08 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The solvent was evaporated from the filtrate, leaving a viscous, yellow oil (1.53 g); $\delta_H(CDCl_3)$ 0.58 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.88 (9 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.32 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.85 (0.8 H, s, *n*-Bu_3SiOH).

Preparation of triethylamine hydrochloride

Excess concentrated hydrochloric acid was added to triethylamine (5.0 cm^3, 3.6 g, 36 mmol) to form the triethylamine hydrochloride product. This was recrystallised from

ethanol and cooled to 0 °C yielded white crystals, m.p. 194–197 °C sublim. (lit.,[62] 261°C dec.).

Reaction between n-Bu_3SiOH and molybdenum pentachloride

$MoCl_5$ (0.50 g, 1.84 mmol) was added to neat *n*-Bu_3SiOH (0.79 g, 3.67 mmol) with no visible reaction until the base, triethylamine (0.96 cm^3, 0.70 g, 3.67 mmol), was added when a white gas formed above the mixture. Most of the dark suspension disappeared leaving only a small deposit on the bottom of the flask. The system was allowed to continue stirring for 60 hours, after which time the precipitate formed was filtered off giving a cream-coloured solid (0.72 g), m.p. 193-196 °C sublim. (Found: C, 36.2; H, 8.6; N, 6.8. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.40 (9 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$), 1.92 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.11 (6 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$).

During the filtration process, a second, intensely blue precipitate formed in the filtrate. This was filtered off and washed with a small amount of benzene, to give a dark blue solid (0.05 g), (Found: C, 14.6; H, 3.6; N, 2.5 %).

The solvent was evaporated from the filtrate and a viscous oil remained (0.63 g); $\delta_H(CDCl_3)$ 0.49 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.87 (9 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.29 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.65 (0.3 H, s, *n*-Bu_3SiOH).

***Heating experiment on* n-Bu_3SiOH**

Neat *n*-Bu_3SiOH (3.00g, 13.9 mmol) was placed in a round-bottomed flask and stirred, with heating, under an inert atmosphere. The liquid was refluxed at 140 °C for 48 hours after which a small sample was removed and the ^1H NMR spectrum was recorded; $\delta_H(CDCl_3)$ 0.52 (6 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.82 (9 H, t, *J* 6.85, $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.25 (12 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$) and 1.69 (1 H, br. s, *n*-Bu_3SiOH).

The base, Et_3N (2.0 cm^3, 2.8 g, 20 mmol), was added to the liquid and the mixture refluxed for a further 24 hours. A small sample was again removed and the ^1H NMR spectrum recorded; $\delta_H(CDCl_3)$ 0.50 (6 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.81 (9 H, t, *J* 6.85, $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.95 (9 H, t, *J* 7.2, $(CH_3CH_2)_3N$), 1.24 (12 H, m, $[CH_3(CH_2)_2CH_2]_3SiOH$), 2.34 (1 H, br. s, *n*-Bu_3SiOH) and 2.48 (6 H, q, *J* 7.2, $(CH_3CH_2)_3N$).

***Reaction between* n-Bu_3SiOH *and titanocene dichloride* (Cp_2TiCl_2)**

Neat *n*-Bu_3SiOH (1.33 g, 6.15 mmol) was added to Cp_2TiCl_2 (Aldrich, 0.50 g, 2.02 mmol), *via* a rubber septum, and the system stirred at room temperature for 45 hours. No reaction was evident so benzene (*ca.* 7 cm^3) as solvent was added and a reflux condensor fitted; the system was heated to 50 °C and maintained at that temperature for two hours with no visible reaction having occurred.

The base, triethylamine (0.75 cm^3, 0.55 g, 5.38 mmol), was added, immediate reaction commenced and after a few minutes dark specks appeared in the solution. The mixture was refluxed and a colour change from red to orange was observed. In

the process a white, puffy substance formed on the surface of the solution which slowly disintegrated and disappeared. After one hour of refluxing, the system was cooled and the solution was stirred overnight. The precipitate was filtered off and washed with benzene (*ca.* 50 cm^3) to give a white powder (0.45 g), m.p. 195–198 °C sublim. (Found: C, 52.2; H, 10.8; N, 10.5. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.38 (9 H, t, *J* 7.3, $(CH_3CH_2)_3NH^+Cl^-$), 1.90 (0.6 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.07 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The filtrate was a clear orange solution. Most of the benzene was evaporated under reduced pressure; the remaining viscous, orange oil was dissolved in dichloromethane and a little hexane added. No precipitation was observed, so all the solvent was removed under reduced pressure and the residual oil was dissolved in hexane and cooling to – 78 °C failed to induce crystallisation. The solvent was evaporated once again and methanol added. The orange-coloured component appeared to separate into the methanol. This component was extracted with methanol (3 × 20 cm^3). All the solvents were evaporated from the viscous oil, from which the red product had been extracted, and analyses were performed (0.85 g); $\delta_H(CDCl_3)$ 0.57 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$), 0.88 (9 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$) and 1.31 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$). Small peaks at δ 6.22 and δ 6.43 ppm.

Recrystallisation of the extracted red product from methanol and dichloromethane was attempted without success. The solvent was removed and no further attempts of recrystallisation were made. Analyses were performed on the crude red powder (0.17 g), m.p. darkening/charring from 70 °C, no melting < 330 °C (Found: C, 34.3; H, 6.1; N, 0 %); δ_H(DMSO) 0.45 (6H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$), 0.80 (9H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$) and 1.21 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$). Small peaks at δ 3.07 (3 H, m) and δ 3.15 (2 H, s) ppm.

***Reaction between* n-Bu_3SiOH *and zirconocene dichloride* (Cp_2ZrCl_2)**

Cp_2ZrCl_2 (Alfa Products, 0.51 g, 1.73 mmol) was placed in a two-necked flask and the system was sealed. THF (*ca.* 20 cm^3) and *n*-Bu_3SiOH (0.75 g, 3.46 mmol) were added with no visible reaction. The base, triethylamine (0.50 cm^3, 0.36 g, 3.6 mmol), was added and the solution immediately appeared to become a gel; addition of THF (*ca.* 50 cm^3) affected the dilution of the thick mixture and a suspension became evident. This mixture was stirred for two days after which the resulting precipitate was allowed to settle. This was filtered, washed with THF and dried in a desiccator to give a white powder (0.44 g), m.p. 196–199 °C sublim. (Found: C, 53.6; H, 11.0; N, 10.0. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.38 (9 H, t, *J* 7.4, $(CH_3CH_2)_3NH^+Cl^-$), 1.88 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.08 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The THF was evaporated from the filtrate and a viscous oil remained (1.15 g) $\delta_H(CDCl_3)$ 0.57 (6 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 0.91 (9 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.32 (12 H, m, $\{[CH_3(CH_2)_2CH_2]_3Si\}_2O$ and $[CH_3(CH_2)_2CH_2]_3SiOH$), 1.56 (0.3 H, s, *n*-Bu_3SiOH) and 6.24 (1 H, s, $(C_5H_5)_2Zr(OSiBu^n{}_3)_2$).

Reactions involving triphenylsilanol (Ph_3SiOH)

Preparation of sodium triphenylsilanoate, $Na^+(OSiPh_3)^-$

A slurry was prepared using NaH (0.12 g, 80 % dispersion in mineral oil, 3.89 mmol) and THF (60 cm^3); this mixture was cooled to -78 °C, Ph_3SiOH (0.97 g, 3.52 mmol) added and the system then allowed to warm to room temperature. A gas was evolved during the warming process. The mixture was stirred for an additional 20 hours, the unreacted NaH then filtered off, washed with THF (2 × 10 cm^3) and neutralised with *iso*-butanol. The THF was evaporated from the filtrate leaving a white powder (1.06 g).

Some of this powder (0.98 g) was dissolved in a minimum of hot ethanol to which a small amount of hexane was added to induce crystallisation. The resulting precipitate was filtered off to give fine, white flakes (0.05 g, 5.5 %), no melting < 600 °C, only charring > 300 °C (lit.,[33] carbonised without melting at 300–350 °C in a vacuum), (Found: C, 64.1; H, 6.0. Calc for $Na^+(OSiPh_3)^-$: C, 72.4; H, 5.1 %); δ_H (CD_3OD) 7.40 (15 H, m, $Na^+[OSi(C_6H_5)_3]^-$).

The solvent from the above filtration, was evaporated from the filtrate leaving a white powder (0.89 g) which was recrystallised from a minimum of hot ethanol to give fine, white flakes (0.09 g, 6.6 %), no melting < 600 °C, only charring > 300 °C (lit.,[33] carbonised without melting at 300–350 °C in a vacuum), (Found: C, 72.3; H, 5.8. Calc. for $Na^+(OSiPh_3)^-$: C, 72.4; H, 5.1 %); δ_H (CD_3OD) 7.33 (15 H, m, $Na^+[OSi(C_6H_5)_3]^-$).

Reactions between Ph_3SiOH and tantalum pentachloride

(a) reaction in solution

Ph_3SiOH (0.50 g, 1.01 mmol) was dissolved in benzene (*ca.* 30 cm^3) and $TaCl_5$ (0.32 g, 0.9 mmol) followed by the base, triethylamine (0.25 cm^3, 0.18 g, 1.8 mmol), were added: an immediate reaction was observed as a white gas gas was clearly visible above the mixture. The mixture was refluxed for 48 hours, cooled and the precipitate allowed to settle. The precipitate was filtered off and washed with benzene (2 × 20 cm^3) to give a white solid (0.43 g), m.p. 194–197 °C sublim., but some remained unmelted < 600 °C (Found: C, 36.5; H, 8.0; N, 7.1. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %).

The solvent was evaporated from the filtrate and a cream-coloured solid remained (0.51 g), m.p. 153–155 °C (lit.,[62] m.p. 153–155 °C) (Found: C, 76.9; H, 5.7. Calc. for Ph_3SiOH: C, 78.2; H, 5.8 %); δ_H ($CDCl_3$) 2.52 (1 H, s, $Ph_3SiO\mathit{H}$) and 7.50 (15 H, m, $[C_6\mathit{H}_5]_3SiOH$).

(b) reaction in solid state

Finely ground Ph_3SiOH (0.49 g, 1.77 mmol) and $TaCl_5$ (0.13 g, 0.36 mmol) were placed into a Schlenk tube and the system was sealed. The reaction vessel was evacuated to 4 mmHg and heated to 110 °C; it was maintained at this temperature for 18 hours. A vacuum sublimation experiment was set up to isolate any product from the reactants: the reaction mixture (0.42 g) was placed in a sublimation tube, the system was sealed and then evacuated to 0.25 mmHg and heated at 110 °C for two days. A small amount of a fine white powder was recovered (0.02 g), (Found: C, 75.1; H, 6.0. Calc. for Ph_3SiOH: C, 78.2; H, 5.8 %); δ_H ($CDCl_3$) 2.52 (1H, s, $Ph_3SiO\mathit{H}$) and 7.41 (15 H, m, $[C_6\mathit{H}_5]_3SiOH$).

Reaction between tantalum pentachloride and triethylamine

Tantalum pentachloride (0.58 g, 1.6 mmol) was placed in a round-bottomed flask containing benzene (*ca.* 50 cm^3) and the system was sealed. The base, triethylamine (1.1 cm^3, 0.82 g, 8.1 mmol), was added via a rubber septum and a reaction was immediately evident with the formation of a white gas above the mixture. The system was heated and the benzene was refluxed for 16 hours. The solid material was filtered off and washed with benzene to give a white solid (0.70 g), m.p. 195–198 °C sublim., but some remained unmelted < 600 °C.

Dichloromethane was added to the solid white material to dissolve the soluble component. The insoluble component was filtered off and washed with CH_2Cl_2. The solvent was removed from the filtrate and various analyses were carried out on the resulting white solid; m.p. 197–199 °C sublim.; $\delta_H(CDCl_3)$ 1.38 (9 H, t, *J* 7.3, $(CH_3CH_2)_3NH^+Cl^-$), 1.88 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.08 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

Preparation of bis(cyclopentadienyl)(triphenylsiloxy)titanium chloride, $Cp_2TiCl(OSiPh_3)$

Ph_3SiOH (0.50 g, 1.81 mmol) was dissolved in benzene (*ca.* 25 cm^3) and Cp_2TiCl_2 (0.23 g, 0.91 mmol) was added with no visible reaction. The system was refluxed and the Cp_2TiCl_2 dissolved completely, after which the base, triethylamine (0.25 cm^3, 0.18 g, 1.80 mmol) was added and after a few moments the reaction commenced as a precipitate began to form. Within one hour the solution had changed from red to orange. The system was refluxed for 48 hours. The precipitate was allowed to settle, filtered off and washed with benzene to give a white solid. (0.13g), m.p.

195–197 °C sublim. (Found: C, 52.9; H, 11.3; N, 10.4. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.38 (9 H, t, *J* 7.3, $(CH_3CH_2)_3NH^+Cl^-$), 1.90 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.07 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The solvent was evaporated from the filtrate leaving an orange-coloured solid; this was recrystallised from a minimum of hot toluene to give an intensely orange-coloured product (0.40 g), m.p. 173–174 °C, reformed, charring from 250 °C (Found: C, 68.9; H, 5.1. Calc. for $C_{28}H_{25}OClSiTi$: C, 68.8; H, 5.15 %); $\delta_H(CDCl_3)$ 6.24 (10 H, s, $(\eta^5\text{-}C_5H_5)_2TiCl(OSiPh_3)$) and 7.20 (15 H, m, $Cp_2TiCl[OSi(C_6H_5)_3]_2$); *m/z* 1072, 995, 917, 876, 718, 634, 553, 488 ($Cp_2TiCl(OSiPh_3)$), 453 ($Cp_2Ti(OSiPh_3)$), 423 ($CpTiCl(OSiPh_3)$), 388 ($CpTi(OSiPh_3)$), 345, 276 ($OSiPh_3$).

Preparation of bis(cyclopentadienyl)bis(triphenylsiloxy)zirconium(II), $Cp_2Zr(OSiPh_3)_2$

Ph_3SiOH (0.50 g, 1.81 mmol) was dissolved in benzene (*ca.* 30 cm^3). Cp_2ZrCl_2 (0.26 g, 0.90 mmol) was added and the system was sealed. There was no visible reaction so the base, triethylamine (0.25 cm^3, 0.18 g, 1.8 mmol) was added. A cloudiness appeared above the solution which became opaque. The solution was refluxed for 48 hours. The resulting precipitate was filtered off and washed with benzene to give a white powder (0.21 g), m.p. slight melting 147–150 °C, 194–196 °C sublim., (Found: C, 56.0; H, 9.8; N, 7.4. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.38 (9 H, t, *J* 7.3, $(CH_3CH_2)_3NH^+Cl^-$), 1.88 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.08 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The benzene was evaporated from the filtrate under reduced pressure leaving a white-coloured residue (0.37 g), a portion of which (0.20 g) was dissolved in a minimum of hot dichloromethane; hexane was added and the system allowed to cool. A precipitate formed which was washed with hexane to give a white powder (0.16 g, 80 %), m.p. 187–190 °C (lit.,[42] m.p. 292–296 °C), (Found: C, 71.3; H, 5.3. Calc. for $C_{46}H_{40}O_2Si_2Zr$: C, 71.5; H, 5.2 %), D (at 19 °C) 1.282(1) g cm^{-3}; $\delta_H(CDCl_3)$ 6.03 (10 H, s, $(\eta^5\text{-}C_5H_5)_2Zr(OSiPh_3)_2$) and 7.32 (30 H, m, $Cp_2Zr[OSi(C_6H_5)_3]_2$), XRF (refer to Figure 1, Chapter 2 – Results and Discussion) and X-ray crystallography (refer to Chapter 3 – X-Ray Crystallography).

Preparation of bis(pentamethylcyclopentadienyl)bis(triphenylsiloxy)zirconium(II), $Cp^*_2Zr(OSiPh_3)_2$

Ph_3SiOH (0.60 g, 2.2 mmol) was dissolved in benzene (*ca.* 30 cm^3) and bis(pentamethylcyclopentadienyl)zirconium dichloride, $Cp^*_2ZrCl_2$ (Strem Chemicals, 0.47 g, 1.1 mmol), was added. There was no visible reaction, so the base, triethylamine (0.3 cm^3, 0.22 g, 2.2 mmol), was added: again, no reaction was observed. The solution was refluxed for 24 hours and the precipitate then allowed to settle; this was filtered off and washed with benzene to give a white solid (0.20 g), m.p. 194–197 °C sublim. (Found: C, 52.6; H, 11.5; N, 10.0. Calc. for $C_6H_{16}ClN$: C, 52.4; H, 11.7; N, 10.2 %); $\delta_H(CDCl_3)$ 1.37 (9 H, t, *J* 7.3, $(CH_3CH_2)_3NH^+Cl^-$), 1.97 (1 H, br. s, $(CH_3CH_2)_3NH^+Cl^-$) and 3.07 (6 H, m, $(CH_3CH_2)_3NH^+Cl^-$).

The benzene was evaporated from the filtrate leaving a yellow/orange solid (1.00 g); $\delta_H(CDCl_3)$ 1.79 (27 H, d, *J* 4.18, $(\eta^5\text{-}C_5Me_5)_2Zr(OSiPh_3)_2$), 1.96 (9 H, s, unreacted $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$) and 7.45 (33 H, m, $Cp^*_2Zr[OSi(C_6H_5)_3]_2$).

A portion of the above solid (0.43 g) was dissolved in a minimum of CH_2Cl_2 and a small volume of hexane added. The solution was cooled at -18 °C for two weeks. The crystals which had grown were separated from the mother liquor by drawing solvent from them with a pasteur pipette. The crystals were washed with hexane to give a mixture of crystals of different physical appearance (0.01 g). The crystals were viewed under a microscope and manually divided into three groups:

a) white, non-crystalline material, m.p. 323–330 °C.

b) white, non-crystalline material with clear crystals attached.

c) clear, crystalline material, m.p. charring from 180 °C, no melting < 600 °C.

Insufficient material was collected from any of these three groups for further analyses, even when the recrystallisation was attempted for a second time.

Preparation of tetrakis(triphenylsiloxy)titanium(IV), $Ti(OSiPh_3)_4$

Ph_3SiOH (1.50 g, 5.42 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and tetra-*n*-butoxytitanium, $Ti(n\text{-}BuO)_4$ (0.50 g, 1.47 mmol), was added. Even before all the butoxide had been added, a fine, white precipitate began forming. The mixture was stirred overnight and the precipitate was filtered off and washed with diethyl ether to give a white powder (1.48 g).

The product appeared insoluble in most solvents, although after a few minutes of boiling in pyridine, it dissolved. This solution was cooled but no crystallisation was evident. In an attempt to achieve crystallisation, some of the product was dissolved in a minimum of hot pyridine and cooled over 24 hours. The vial containing this solution was placed in an oil bath at 120 °C and the temperature was gradually decreased over 24 hours. No crystallisation was evident, so the lid of the vial was

perforated to allow slow evaporation of some of the pyridine and promote crystal growth. The vial was left for about two weeks after which time the volume had decreased only slightly. Closer inspection revealed that a gel had formed. More pyridine was added but the gel did not become diluted; it simply became a dispersion of gel globules.

Using a different experimental arrangement, attempts were made to purify and grow crystals of the reaction product. A sublimation experiment was set up which involved heating a cylindrical aluminium block (∅ 15 cm) with two Bunsen burners (refer to Figure 2, Chapter 2 – Results and Discussion). A hole was bored into the top of the cylinder to accommodate a cold finger sublimation tube. A small hole was drilled into the side for the thermocouple probe. The burners and aluminium block were insulated with fire bricks.

a) Some of the white reaction product (0.29 g) was placed in the cold finger sublimation tube and heated at 380 °C and 1 mmHg for a few hours. Sublimation did occur, but no crystals were formed on the tip of the cold finger. A pure white powder was collected from the experiment (0.02 g).

b) Similar to (a), 0.21 g of white product was used and was heated at 350 °C for 4 hours. This yielded 0.06 g of sublimed product.

The sublimation experiment was set up using a hot-plate instead of Bunsen burners.

c) Similar to (a), 0.19 g of white product was used and was heated at 350 °C for 10 hours. This yielded 0.05 g of sublimed product.

Various analyses were performed on the combined pure sublimed products (0.13 g), m.p. 505–506 °C (lit.,[76] m.p. 501–505 °C in sealed tubes and 460–470 °C dec. in open tubes), (Found: C, 75.3; H, 5.2. Calc for $C_{72}H_{60}O_4Si_4Ti$: C, 75.2; H, 5.3 %).

Reactions involving diphenylsilanediol ($Ph_2Si(OH)_2$)

Preparation of hexadecaphenyloctasiloxyspiro(9,9)titanium(IV) *{$\widetilde{Ti[OSiPh_2(OSiPh_2)_3O]_2}$}*

Diphenylsilanediol, $Ph_2Si(OH)_2$ (10.00 g, 46.2 mmol), was added to diethyl ether (*ca.* 100 cm^3) in a round-bottomed flask and the system was sealed. $Ti(n\text{-}BuO)_4$ (8.00 g, 23.5 mmol) was added; an immediate reaction was observed and the suspension of $Ph_2Si(OH)_2$ disappeared within a few minutes. The solution was refluxed for 72 hours. The solvent was evaporated as no precipitate had formed and an orange-coloured oil remained. Hexane was added and the surface of the glass in contact with the oil was scratched with a glass rod to promote crystallisation. Eventually all the oil was converted in this manner to a fine, white powder (2.02 g).

Some of the powder (1.83 g) was recrystallised from hot diethyl ether yielding good quality crystals (0.97 g, 11.2 %), m.p. 310–313 °C (lit.,[77] 314–314.5 °C), D (at 22 ° C) 1.176 (6) g cm^{-3}, (Found: C, 69.2; H, 4.8. Calc for $C_{96}H_{80}O_{10}Si_8Ti$: C, 69.2; H, 4.8 %); $\delta_H(CDCl_3)$ 7.19 (5 H, m, $Ti\{OSi(C_6H_5)_2[OSi(C_6H_5)_2]_3O\}_2$). A complete crystal structure analysis was performed on this crystalline material (refer to Chapter 3 – X-Ray Crystallography).

Some of this crystalline material (0.13 g) was dissolved in a minimum of hot toluene and set aside to allow crystallisation. After a few days, good quality crystals, m.p. 314–315 °C (lit.,[77] 287–303 °C) were removed from the mother liquor and washed with hexane. A few high quality crystals were selected and oscillation X-ray photographs were taken to establish whether the unit cell dimensions differed from those observed above (refer to Chapter 2 - Results and Discussion)

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Appendix

Table 1 - Fractional atomic coordinates (x 10^4) and thermal motion parameters ($Å^2$ x 10^3) with estimated standard deviations in parentheses for the least significant figure(s).

$$U_{equiv} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i . a_j$$

Atom	x/a	y/b	z/c	U_{iso}/U_{equiv}(*)
TI(1)	7158 (1)	2387 (1)	9027 (1)	33 (1) *
O(1)	7808 (4)	2491 (2)	9707 (2)	46 (2) *
SI(1)	8497 (2)	2737 (1)	10222 (1)	38 (1) *
C(1)	9752 (6)	2768 (3)	9997 (4)	41 (3)
C(2)	9982 (7)	2676 (3)	9459 (4)	49 (3)
C(3)	10937 (8)	2682 (4)	9305 (5)	71 (4)
C(4)	11663 (9)	2808 (4)	9710 (5)	80 (4)
C(5)	11472 (9)	2899 (4)	10255 (5)	84 (4)
C(6)	10500 (8)	2881 (4)	10404 (5)	71 (4)
C(7)	8455 (6)	2385 (4)	10884 (4)	43 (3)
C(8)	8476 (7)	2613 (4)	11422 (5)	68 (3)
C(9)	8528 (8)	2330 (5)	11918 (5)	77 (4)
C(10)	8514 (8)	1840 (5)	11878 (5)	84 (4)
C(11)	8498 (9)	1597 (5)	11362 (6)	96 (4)
C(12)	8472 (7)	1879 (4)	10860 (5)	60 (3)
O(2)	8111 (4)	3278 (2)	10338 (3)	51 (3) *
SI(2)	7194 (2)	3635 (1)	10375 (1)	43 (1) *
C(13)	7518 (7)	4080 (4)	10951 (4)	53 (3)
C(14)	8463 (8)	4146 (4)	11162 (5)	74 (4)
C(15)	8676(10)	4499 (5)	11593 (6)	99 (5)
C(16)	7965(10)	4769 (5)	11772 (6)	108 (5)
C(17)	7038(10)	4723 (5)	11589 (6)	103 (5)
C(18)	6804 (9)	4369 (4)	11161 (5)	84 (4)
C(19)	6082 (6)	3297 (3)	10500 (4)	35 (2)
C(20)	5870 (7)	3134 (4)	11032 (4)	57 (3)
C(21)	5001 (8)	2895 (4)	11125 (5)	69 (3)
C(22)	4354 (8)	2794 (4)	10673 (5)	72 (4)
C(23)	4541 (8)	2945 (4)	10128 (5)	80 (4)
C(24)	5409 (7)	3203 (4)	10046 (5)	63 (3)
O(3)	6991 (4)	3920 (2)	9780 (3)	50 (3) *
SI(3)	7240 (2)	4208 (1)	9214 (1)	46 (1) *
C(25)	6644 (8)	4813 (4)	9207 (5)	68 (3)
C(26)	6569(10)	5068 (6)	9704 (6)	115 (5)
C(27)	6145(11)	5557 (6)	9695 (7)	139 (6)
C(28)	5827(10)	5708 (5)	9172 (7)	118 (5)
C(29)	5823(10)	5486 (5)	8659 (6)	109 (5)
C(30)	6280 (8)	5006 (5)	8678 (6)	88 (4)
C(31)	8575 (8)	4251 (4)	9199 (5)	71 (4)
C(32)	9106(10)	3892 (5)	9001 (5)	103 (5)
C(33)	10159(11)	3910 (6)	8999 (6)	127 (6)
C(34)	10572(11)	4318 (6)	9209 (7)	132 (6)
C(35)	10081(12)	4737 (6)	9316 (6)	138 (6)
C(36)	9021(10)	4712 (5)	9320 (6)	112 (5)
O(4)	6811 (4)	3911 (2)	8657 (3)	52 (3) *
SI(4)	6332 (2)	3427 (1)	8375 (1)	40 (1) *
C(37)	5003 (6)	3426 (3)	8441 (4)	42 (3)
C(38)	4479 (7)	2999 (4)	8440 (4)	51 (3)
C(39)	3474 (8)	3007 (4)	8487 (4)	63 (3)
C(40)	2992 (8)	3425 (4)	8529 (4)	65 (3)
C(41)	3497 (9)	3861 (5)	8531 (5)	84 (4)

Table 1 - Continued.

C(42)	4499 (8)	3865 (4)	8484 (4)	65 (3)
C(43)	6676 (6)	3407 (3)	7634 (4)	43 (3)
C(44)	6339 (8)	3041 (5)	7264 (5)	82 (4)
C(45)	6661 (9)	3013 (5)	6705 (6)	106 (5)
C(46)	7321 (9)	3343 (5)	6539 (6)	92 (4)
C(47)	7664 (8)	3698 (4)	6882 (5)	84 (4)
C(48)	7343 (7)	3735 (4)	7436 (5)	62 (3)
O(5)	6761 (4)	2947 (2)	8711 (3)	48 (3) *
O(6)	6136 (4)	2006 (2)	9102 (2)	40 (2) *
SI(5)	5565 (2)	1504 (1)	9226 (1)	39 (1) *
C(49)	5371 (6)	1494 (3)	9993 (4)	38 (3)
C(50)	4685 (8)	1183 (4)	10186 (5)	72 (4)
C(51)	4572 (8)	1140 (4)	10781 (5)	86 (4)
C(52)	5144 (9)	1423 (5)	11149 (5)	89 (4)
C(53)	5838 (8)	1731 (4)	10972 (5)	70 (4)
C(54)	5935 (7)	1756 (4)	10380 (4)	58 (3)
C(55)	4397 (7)	1471 (4)	8783 (4)	46 (3)
C(56)	3552 (8)	1672 (4)	8971 (5)	67 (3)
C(57)	2654 (9)	1631 (4)	8629 (5)	81 (4)
C(58)	2651 (9)	1423 (5)	8125 (6)	91 (4)
C(59)	3441(10)	1222 (5)	7913 (6)	104 (5)
C(60)	4348 (8)	1256 (4)	8267 (5)	75 (4)
O(7)	6244 (4)	1061 (2)	9047 (3)	47 (3) *
SI(6)	6831 (2)	572 (1)	8922 (1)	42 (1) *
C(61)	6197 (7)	220 (4)	8323 (4)	53 (3)
C(62)	5374 (9)	-30 (5)	8425 (5)	89 (4)
C(63)	4882(11)	-315 (5)	7966 (6)	120 (5)
C(64)	5294 (9)	-323 (5)	7471 (6)	97 (4)
C(65)	6063 (9)	-68 (5)	7342 (6)	98 (5)
C(66)	6556 (8)	218 (4)	7788 (5)	77 (4)
C(67)	6989 (6)	212 (4)	9575 (4)	47 (3)
C(68)	7404 (7)	-255 (4)	9573 (5)	67 (3)
C(69)	7580 (8)	-526 (4)	10071 (5)	82 (4)
C(70)	7346 (8)	-357 (5)	10563 (5)	86 (4)
C(71)	6959 (9)	97 (5)	10613 (6)	111 (5)
C(72)	6804 (8)	389 (5)	10104 (5)	92 (4)
O(8)	7876 (4)	718 (2)	8702 (3)	52 (3) *
SI(7)	9002 (2)	864 (1)	8705 (1)	40 (1) *
C(73)	9642 (6)	372 (3)	8347 (4)	39 (3)
C(74)	10626 (8)	443 (4)	8275 (5)	71 (4)
C(75)	11174 (9)	69 (4)	8038 (5)	83 (4)
C(76)	10736 (8)	-347 (4)	7865 (4)	67 (3)
C(77)	9789 (8)	-429 (4)	7925 (5)	73 (4)
C(78)	9251 (7)	-69 (4)	8178 (4)	54 (3)
C(79)	9549 (6)	972 (3)	9442 (4)	41 (3)
C(80)	10091 (7)	1385 (4)	9586 (5)	64 (3)
C(81)	10512 (8)	1453 (4)	10151 (5)	72 (4)
C(82)	10368 (8)	1110 (4)	10539 (5)	75 (4)
C(83)	9846 (7)	691 (4)	10414 (5)	68 (3)
C(84)	9450 (7)	623 (4)	9861 (4)	55 (3)
O(9)	9090 (4)	1358 (2)	8338 (3)	47 (3) *
SI(8)	8515 (2)	1825 (1)	8077 (1)	39 (1) *
C(85)	9437 (6)	2255 (3)	7843 (4)	38 (3)
C(86)	9224 (7)	2740 (4)	7786 (4)	63 (3)
C(87)	9933 (9)	3082 (4)	7634 (5)	81 (4)
C(88)	10842 (8)	2919 (4)	7539 (5)	69 (3)
C(89)	11061 (8)	2445 (4)	7592 (4)	68 (3)
C(90)	10367 (7)	2107 (4)	7752 (4)	59 (3)
C(91)	7610 (7)	1632 (3)	7508 (4)	49 (3)
C(92)	6618 (8)	1681 (4)	7534 (5)	78 (4)
C(93)	5947(10)	1526 (5)	7086 (6)	97 (4)

Table 1 - Continued.

C(94)	6257 (9)	1305 (5)	6627 (5)	89 (4)
C(95)	7224(12)	1241 (6)	6580 (7)	138 (6)
C(96)	7887(10)	1433 (5)	7024 (6)	106 (5)
O(10)	7932 (4)	2088 (2)	8561 (3)	48 (3) *

Anisotropic atoms have thermal parameters (Å^2 x 10^3) of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
TI(1)	30 (1)	34 (1)	34 (1)	4 (1)	3 (1)	2 (1)
O(1)	39 (4)	56 (5)	41 (4)	-1 (3)	-7 (3)	0 (3)
SI(1)	31 (2)	46 (2)	38 (2)	1 (2)	1 (1)	3 (1)
O(2)	44 (4)	54 (5)	56 (5)	-11 (4)	6 (4)	10 (4)
SI(2)	42 (2)	40 (2)	46 (2)	0 (2)	5 (2)	1 (2)
O(3)	56 (5)	49 (5)	44 (4)	11 (4)	0 (4)	0 (4)
SI(3)	46 (2)	39 (2)	52 (2)	1 (2)	3 (2)	-2 (2)
O(4)	56 (5)	43 (5)	56 (5)	8 (4)	-9 (4)	-4 (4)
SI(4)	38 (2)	37 (2)	42 (2)	7 (2)	0 (1)	0 (2)
O(5)	42 (4)	46 (4)	54 (5)	10 (4)	-5 (4)	3 (3)
O(6)	35 (4)	46 (4)	39 (4)	1 (3)	3 (3)	-8 (3)
SI(5)	30 (2)	43 (2)	45 (2)	4 (2)	5 (1)	1 (1)
O(7)	40 (4)	55 (5)	45 (4)	2 (4)	6 (3)	10 (4)
SI(6)	36 (2)	45 (2)	44 (2)	1 (2)	2 (1)	2 (2)
O(8)	39 (4)	67 (5)	51 (5)	2 (4)	10 (4)	1 (4)
SI(7)	34 (2)	48 (2)	38 (2)	3 (2)	4 (1)	9 (2)
O(9)	36 (4)	46 (5)	58 (5)	11 (4)	5 (3)	8 (3)
SI(8)	36 (2)	43 (2)	38 (2)	4 (2)	5 (1)	4 (1)
O(10)	37 (4)	54 (5)	54 (5)	-5 (4)	16 (3)	0 (3)

Fractional atomic coordinates (x 10^4) for the hydrogen atoms, with estimated standard deviations for the least significant figure(s).

Parent atom	H	x/a	y/b	z/c
C(2)	H(2)	9448 (7)	2597 (3)	9162 (4)
C(3)	H(3)	11088 (8)	2600 (4)	8906 (5)
C(4)	H(4)	12347 (9)	2828 (4)	9600 (5)
C(5)	H(5)	12007 (9)	2982 (4)	10549 (5)
C(6)	H(6)	10348 (8)	2948 (4)	10806 (5)
C(8)	H(8)	8458 (7)	2976 (4)	11449 (5)
C(9)	H(9)	8572 (8)	2491 (5)	12300 (5)
C(10)	H(10)	8521 (8)	1644 (5)	12236 (5)
C(11)	H(11)	8505 (9)	1235 (5)	11345 (6)
C(12)	H(12)	8467 (7)	1709 (4)	10483 (5)
C(14)	H(14)	8995 (8)	3943 (4)	11020 (5)
C(15)	H(15)	9358(10)	4544 (5)	11762 (6)
C(16)	H(16)	8138(10)	5031 (5)	12056 (6)
C(17)	H(17)	6518(10)	4922 (5)	11751 (6)

Table 1 - Continued.

C(18)	H(18)	6115 (9)	4329 (4)	11006 (5)
C(20)	H(20)	6352 (7)	3190 (4)	11366 (4)
C(21)	H(21)	4858 (8)	2799 (4)	11519 (5)
C(22)	H(22)	3744 (8)	2611 (4)	10730 (5)
C(23)	H(23)	4070 (8)	2878 (4)	9793 (5)
C(24)	H(24)	5541 (7)	3313 (4)	9654 (6)
C(26)	H(26)	6791(10)	4915 (6)	10078 (6)
C(27)	H(27)	6122(11)	5758 (6)	10049 (7)
C(28)	H(28)	5533(10)	6039 (5)	9163 (7)
C(29)	H(29)	5534(10)	5635 (5)	8297 (6)
C(30)	H(30)	6334 (8)	4819 (5)	8316 (6)
C(32)	H(32)	8766(10)	3592 (5)	8853 (5)
C(33)	H(33)	10545(11)	3638 (6)	8846 (6)
C(34)	H(34)	11294(11)	4322 (6)	9288 (7)
C(35)	H(35)	10430(12)	5049 (6)	9405 (6)
C(36)	H(36)	8631(10)	5008 (5)	9394 (6)
C(38)	H(38)	4822 (7)	2682 (4)	8404 (4)
C(39)	H(39)	3112 (8)	2693 (4)	8493 (4)
C(40)	H(40)	2272 (8)	3422 (4)	8558 (4)
C(41)	H(41)	3138 (9)	4173 (5)	8571 (5)
C(42)	H(42)	4853 (8)	4183 (4)	8477 (4)
C(44)	H(44)	5861 (8)	2798 (5)	7391 (5)
C(45)	H(45)	6414 (9)	2752 (5)	6434 (6)
C(46)	H(46)	7558 (9)	3314 (5)	6149 (6)
C(47)	H(47)	8138 (8)	3938 (4)	6745 (5)
C(48)	H(48)	7597 (7)	4003 (4)	7693 (5)
C(50)	H(50)	4264 (8)	988 (4)	9907 (5)
C(51)	H(51)	4084 (8)	910 (4)	10924 (5)
C(52)	H(52)	5042 (9)	1408 (5)	11566 (5)
C(53)	H(53)	6269 (8)	1922 (4)	11251 (5)
C(54)	H(54)	6431 (7)	1983 (4)	10240 (4)
C(56)	H(56)	3567 (8)	1846 (4)	9346 (5)
C(57)	H(57)	2036 (9)	1757 (4)	8770 (5)
C(58)	H(58)	2027 (9)	1415 (5)	7878 (6)
C(59)	H(59)	3409(10)	1056 (5)	7534 (6)
C(60)	H(60)	4951 (8)	1113 (4)	8126 (5)
C(62)	H(62)	5113 (9)	-20 (5)	8811 (5)
C(63)	H(63)	4267(11)	-495 (5)	8020 (6)
C(64)	H(64)	5000 (9)	-545 (5)	7167 (6)
C(65)	H(65)	6282 (9)	-72 (5)	6946 (6)
C(66)	H(66)	7151 (8)	407 (4)	7712 (5)
C(68)	H(68)	7558 (7)	-398 (4)	9199 (5)
C(69)	H(69)	7907 (8)	-849 (4)	10050 (5)
C(70)	H(70)	7442 (8)	-569 (5)	10910 (5)
C(71)	H(71)	6795 (9)	225 (5)	10992 (6)
C(72)	H(72)	6554 (8)	728 (5)	10134 (5)
C(74)	H(74)	10944 (8)	760 (4)	8380 (5)
C(75)	H(75)	11887 (9)	111 (4)	8005 (5)
C(76)	H(76)	11123 (8)	-604 (4)	7684 (4)
C(77)	H(77)	9479 (8)	-741 (4)	7791 (5)
C(78)	H(78)	8552 (7)	-134 (4)	8235 (4)
C(80)	H(80)	10190 (7)	1635 (4)	9288 (5)
C(81)	H(81)	10903 (8)	1750 (4)	10254 (5)
C(82)	H(82)	10650 (8)	1163 (4)	10940 (5)
C(83)	H(83)	9763 (7)	440 (4)	10714 (5)
C(84)	H(84)	9082 (7)	318 (4)	9761 (4)
C(86)	H(86)	8554 (7)	2856 (4)	7848 (4)
C(87)	H(87)	9767 (9)	3435 (4)	7602 (5)
C(88)	H(88)	11346 (8)	3154 (4)	7426 (5)
C(89)	H(89)	11730 (8)	2330 (4)	7526 (4)
C(90)	H(90)	10545 (7)	1756 (4)	7790 (4)

Table 1 - Continued.

C(92)	H(92)	6372 (8)	1837 (4)	7878 (5)
C(93)	H(93)	5236(10)	1577 (5)	7117 (6)
C(94)	H(94)	5776 (9)	1181 (5)	6320 (5)
C(95)	H(95)	7460(12)	1075 (6)	6238 (7)
C(96)	H(96)	8598(10)	1412 (5)	6973 (6)

Table 2 - Observed and calculated structure factors for $C_{96}H_{80}O_{10}Si_8Ti$

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
2	0	0	50	-53	7	3	0	57	-55	3	7	0	137	-141	8	10	0	29	16	4	14	0	26	27
4	0	0	74	-73	8	3	0	96	-94	4	7	0	121	-115	11	10	0	24	27	5	14	0	93	95
6	0	0	41	46	12	3	0	32	35	6	7	0	49	49	12	10	0	24	16	6	14	0	32	-32
10	0	0	45	-41	1	4	0	114	-117	7	7	0	91	93	13	10	0	25	-29	9	14	0	48	-43
12	0	0	34	-39	3	4	0	67	70	8	7	0	58	-55	14	10	0	34	-29	11	14	0	30	26
14	0	0	51	46	4	4	0	99	-95	9	7	0	33	33	1	11	0	107	109	1	15	0	50	51
16	0	0	37	-32	6	4	0	91	86	10	7	0	52	57	3	11	0	113	-110	2	15	0	36	-34
1	1	0	60	53	7	4	0	34	30	13	7	0	20	22	4	11	0	115	104	3	15	0	61	-58
2	1	0	15	-8	9	4	0	23	-32	0	8	0	49	52	6	11	0	62	64	5	15	0	65	66
3	1	0	60	-60	11	4	0	48	42	1	8	0	82	-79	8	11	0	20	-7	7	15	0	47	-44
6	1	0	50	-56	13	4	0	35	34	2	8	0	30	-31	12	11	0	33	-31	8	15	0	56	-63
7	1	0	67	-59	2	5	0	129	126	4	8	0	97	100	14	11	0	22	-7	9	15	0	53	47
8	1	0	103	110	4	5	0	212	212	5	8	0	56	-55	1	12	0	43	-45	12	15	0	44	46
9	1	0	37	41	5	5	0	68	-66	6	8	0	57	-55	2	12	0	121	-121	13	15	0	36	33
10	1	0	43	-43	6	5	0	51	-49	7	8	0	80	84	3	12	0	27	22	0	16	0	49	-47
12	1	0	37	-36	7	5	0	98	112	11	8	0	31	-44	4	12	0	73	-68	1	16	0	40	-37
14	1	0	30	27	8	5	0	47	45	12	8	0	29	-34	5	12	0	123	-119	2	16	0	70	-68
16	1	0	27	23	9	5	0	88	-93	14	8	0	23	29	6	12	0	30	-35	3	16	0	100	97
0	2	0	176	-175	10	5	0	26	37	1	9	0	113	-108	7	12	0	48	-50	4	16	0	22	-13
1	2	0	79	-82	12	5	0	28	-32	2	9	0	66	-65	8	12	0	53	48	3	17	0	45	48
3	2	0	287	298	0	6	0	175	172	4	9	0	43	41	9	12	0	94	94	5	17	0	68	-70
4	2	0	76	78	1	6	0	191	191	5	9	0	32	23	11	12	0	20	-24	6	17	0	45	-47
5	2	0	43	-44	2	6	0	52	51	6	9	0	29	-32	14	12	0	22	19	7	17	0	41	40
6	2	0	66	-61	4	6	0	96	-90	7	9	0	65	-61	1	13	0	32	-32	8	17	0	37	39
9	2	0	44	-49	5	6	0	35	34	9	9	0	71	-73	4	13	0	51	-52	9	17	0	53	-49
10	2	0	55	50	6	6	0	43	43	10	9	0	38	-36	5	13	0	36	-40	10	17	0	25	-21
14	2	0	57	-60	7	6	0	46	46	11	9	0	43	52	7	13	0	22	15	0	18	0	17	4
16	2	0	33	30	8	6	0	31	23	13	9	0	42	-38	8	13	0	32	40	1	18	0	35	32
1	3	0	36	-39	9	6	0	35	-36	0	10	0	82	-84	9	13	0	89	89	2	18	0	35	34
2	3	0	46	45	10	6	0	58	-54	1	10	0	22	-17	11	13	0	26	21	3	18	0	52	-52
3	3	0	170	172	13	6	0	23	-27	2	10	0	66	68	0	14	0	35	42	4	18	0	62	-54
4	3	0	201	199	16	6	0	32	32	3	10	0	37	-38	1	14	0	26	-22	5	18	0	57	-61
5	3	0	153	-145	1	7	0	122	-126	4	10	0	140	-132	2	14	0	44	46	6	18	0	69	66
6	3	0	62	-60	2	7	0	146	-143	6	10	0	48	46	3	14	0	34	-30	8	18	0	22	-29

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
10	18	0	28	-26	-11	0	1	72	67	-12	2	1	21	9	15	3	1	44	-48	5	5	1	94	-95
2	19	0	26	18	-9	0	1	56	-51	-10	2	1	38	-35	-14	4	1	24	-25	6	5	1	41	-35
5	19	0	40	45	-7	0	1	125	128	-9	2	1	55	60	-11	4	1	46	-37	7	5	1	51	61
8	19	0	35	33	-5	0	1	58	-60	-8	2	1	28	29	-9	4	1	37	-31	8	5	1	24	-30
12	19	0	30	-28	-3	0	1	139	144	-7	2	1	80	-85	-7	4	1	73	69	9	5	1	29	-24
1	20	0	24	-22	-1	0	1	237	234	-6	2	1	140	-134	-6	4	1	91	-87	10	5	1	32	31
2	20	0	35	37	1	0	1	311	-318	-5	2	1	137	-131	-5	4	1	57	53	14	5	1	30	29
3	20	0	46	-41	3	0	1	130	121	-4	2	1	18	22	-4	4	1	207	-209	15	5	1	35	36
5	20	0	45	44	5	0	1	120	-125	-3	2	1	399	402	-1	4	1	62	64	-12	6	1	20	-22
10	20	0	22	-1	7	0	1	179	183	-2	2	1	103	-106	0	4	1	93	92	-11	6	1	25	-30
11	20	0	25	-11	9	0	1	37	-39	0	2	1	98	91	1	4	1	193	208	-9	6	1	107	104
2	21	0	110	-119	13	0	1	41	42	2	2	1	56	-54	2	4	1	146	-139	-8	6	1	59	-57
4	21	0	17	8	15	0	1	22	-12	3	2	1	129	121	4	4	1	32	-26	-7	6	1	18	-36
5	21	0	48	-52	-15	1	1	38	-44	4	2	1	152	-147	5	4	1	28	-35	-6	6	1	48	46
6	21	0	40	41	-9	1	1	64	57	5	2	1	74	-75	6	4	1	163	160	-5	6	1	45	-44
8	21	0	47	-50	-8	1	1	46	-52	6	2	1	56	-58	7	4	1	38	-33	-4	6	1	26	-26
10	21	0	24	23	-7	1	1	76	-71	7	2	1	80	-78	8	4	1	38	-40	-3	6	1	75	75
1	22	0	62	65	-4	1	1	75	76	8	2	1	76	-82	10	4	1	59	52	-2	6	1	26	27
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7	22	0	20	21	-2	1	1	133	137	10	2	1	59	57	13	4	1	41	32	1	6	1	261	-257
6	23	0	47	-48	-1	1	1	339	-349	13	2	1	50	-53	-11	5	1	28	-34	2	6	1	216	-210
7	23	0	55	-56	1	1	1	306	303	-12	3	1	20	9	-9	5	1	22	-23	3	6	1	128	-123
8	23	0	26	27	2	1	1	94	91	-10	3	1	36	41	-8	5	1	45	49	4	6	1	95	96
9	23	0	41	39	3	1	1	262	256	-9	3	1	77	75	-7	5	1	60	-62	5	6	1	176	167
3	24	0	27	28	4	1	1	107	110	-6	3	1	76	72	-6	5	1	74	-76	6	6	1	28	26
5	24	0	49	-50	5	1	1	163	-160	-5	3	1	26	29	-4	5	1	39	-36	7	6	1	52	-51
6	24	0	38	-37	6	1	1	66	-60	-4	3	1	145	145	-3	5	1	171	177	8	6	1	34	34
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2	26	0	35	30	11	1	1	86	82	-1	3	1	87	-87	0	5	1	60	-65	12	6	1	40	-37
9	26	0	26	-23	13	1	1	32	-31	0	3	1	56	55	1	5	1	331	333	-15	7	1	40	28
3	27	0	34	-38	14	1	1	44	-47	5	3	1	34	-35	2	5	1	229	-230	-11	7	1	34	-28
5	27	0	24	28	15	1	1	28	21	9	3	1	20	-21	3	5	1	115	-112	-10	7	1	93	-91
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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-3	7	1	140	-148	-4	9	1	30	-26	-3	11	1	59	59	0	13	1	35	-35	-4	16	1	58	65
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0	7	1	207	205	-1	9	1	46	-50	0	11	1	24	-16	4	13	1	23	21	3	16	1	76	81
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3	7	1	217	214	2	9	1	43	42	4	11	1	50	-49	-12	14	1	25	-31	10	16	1	46	43
4	7	1	37	45	3	9	1	34	31	7	11	1	45	-43	-6	14	1	40	37	-12	17	1	27	-23
7	7	1	55	57	6	9	1	97	-95	8	11	1	73	73	-5	14	1	20	-17	-8	17	1	32	35
8	7	1	48	-45	7	9	1	62	62	13	11	1	37	33	-3	14	1	21	21	-7	17	1	57	61
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12	7	1	29	27	13	9	1	53	-53	-5	12	1	38	37	3	14	1	67	-67	-3	17	1	28	23
13	7	1	40	37	-14	10	1	34	27	-4	12	1	52	-52	4	14	1	69	63	-2	17	1	108	-107
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7	8	1	64	64	-14	11	1	27	19	-6	13	1	69	-67	9	15	1	46	50	2	18	1	45	-42
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-10	9	1	21	-21	-6	11	1	42	38	-3	13	1	29	-33	-12	16	1	23	15	7	18	1	58	-54
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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-5	19	1	31	33	-2	23	1	64	66	-10	1	2	42	43	-9	3	2	30	-26	11	4	2	37	-35
4	19	1	55	58	4	23	1	42	-40	-8	1	2	85	-91	-7	3	2	120	127	12	4	2	27	31
5	19	1	56	-60	7	23	1	42	40	-7	1	2	45	43	-6	3	2	82	78	14	4	2	36	42
10	19	1	30	-29	8	23	1	32	26	-6	1	2	49	47	-5	3	2	53	-59	-16	5	2	28	-26
-8	20	1	24	-20	-10	24	1	22	-23	-5	1	2	75	77	-4	3	2	203	-202	-13	5	2	39	-44
-4	20	1	59	51	-8	24	1	32	26	-4	1	2	47	49	-3	3	2	147	-144	-11	5	2	36	45
-3	20	1	46	44	-7	24	1	45	-46	-3	1	2	50	52	-2	3	2	115	113	-10	5	2	53	53
-2	20	1	22	24	-4	24	1	39	-41	-1	1	2	49	57	-1	3	2	105	103	-9	5	2	29	-17
-1	20	1	48	-53	-3	24	1	28	-31	0	1	2	266	272	0	3	2	124	126	-8	5	2	25	-29
1	20	1	58	-57	0	24	1	31	58	1	1	2	101	-101	1	3	2	101	99	-6	5	2	87	-85
7	20	1	55	-50	6	24	1	46	44	2	1	2	104	-106	2	3	2	40	34	-5	5	2	62	-64
9	20	1	36	38	8	24	1	22	-13	3	1	2	42	40	3	3	2	97	-97	-3	5	2	43	40
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0	21	1	41	75	4	28	1	35	-32	-5	2	2	46	47	-12	4	2	41	37	5	5	2	102	-98
1	21	1	86	-87	7	29	1	24	11	-4	2	2	52	-57	-11	4	2	35	-36	8	5	2	18	-15
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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3	6	2	107	101	3	8	2	64	63	4	10	2	47	-43	3	12	2	79	-81	4	14	2	53	54
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6	6	2	100	-105	7	8	2	114	120	8	10	2	19	17	7	12	2	93	-93	10	14	2	51	-49
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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2	17	2	46	-40	-1	21	2	42	45	-4	27	2	23	21	-2	1	3	28	33	-4	3	3	32	28
3	17	2	82	80	0	21	2	66	71	-3	27	2	29	31	-1	1	3	53	-56	-2	3	3	125	-128
4	17	2	39	37	1	21	2	64	-59	-1	27	2	59	-61	0	1	3	72	-65	-1	3	3	148	145
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1	19	2	31	36	5	23	2	36	36	-5	0	3	236	230	-3	2	3	166	167	-4	4	3	54	-52
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5	19	2	45	-42	-1	24	2	41	43	-1	0	3	71	74	-1	2	3	53	54	-2	4	3	176	-178
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7	19	2	22	-27	3	24	2	21	9	3	0	3	24	23	1	2	3	161	-167	1	4	3	158	-153
8	19	2	36	30	-10	25	2	26	15	7	0	3	88	82	2	2	3	166	-158	2	4	3	88	87
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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8	4	3	51	53	-1	6	3	309	-308	3	8	3	33	-31	-2	10	3	111	-106	4	12	3	50	50
9	4	3	66	68	0	6	3	176	172	4	8	3	42	41	-1	10	3	21	24	6	12	3	54	-55
11	4	3	36	-33	1	6	3	259	262	5	8	3	24	24	1	10	3	53	-56	8	12	3	100	102
13	4	3	26	17	2	6	3	131	132	6	8	3	43	37	5	10	3	26	-22	9	12	3	31	25
14	4	3	35	-33	3	6	3	16	-16	7	8	3	22	25	6	10	3	76	-80	10	12	3	30	42
15	4	3	47	-44	4	6	3	107	102	8	8	3	92	-91	9	10	3	59	-55	11	12	3	66	-53
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1	5	3	212	-214	-3	7	3	134	-127	-4	9	3	22	-15	0	11	3	16	14	0	13	3	47	-44
2	5	3	135	-131	-1	7	3	74	79	-3	9	3	52	49	1	11	3	26	-23	4	13	3	31	-35
3	5	3	206	198	0	7	3	114	117	-1	9	3	105	-105	2	11	3	38	-31	5	13	3	46	-44
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5	5	3	165	-173	2	7	3	22	16	1	9	3	86	91	4	11	3	116	114	8	13	3	33	26
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11	5	3	31	-25	8	7	3	28	-26	6	9	3	20	11	10	11	3	28	-28	-6	14	3	28	-23
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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-3	15	3	31	-26	-6	18	3	22	-15	-1	22	3	107	-110	-6	0	4	104	-96	1	2	4	301	-306
2	15	3	84	82	-3	18	3	51	-57	0	22	3	54	54	-4	0	4	128	127	2	2	4	207	-202
3	15	3	82	-82	-2	18	3	80	-78	3	22	3	39	39	-2	0	4	45	-41	4	2	4	83	77
7	15	3	53	60	0	18	3	40	-47	5	22	3	26	30	0	0	4	202	-212	5	2	4	22	26
8	15	3	36	31	1	18	3	76	80	8	22	3	44	-36	2	0	4	315	305	7	2	4	35	-32
9	15	3	48	41	2	18	3	67	-74	-10	23	3	26	18	4	0	4	91	91	11	2	4	24	-21
10	15	3	42	-41	3	18	3	56	-50	-3	23	3	22	19	6	0	4	122	113	-9	3	4	44	-42
13	15	3	23	-5	4	18	3	48	54	-2	23	3	29	29	10	0	4	79	-75	-8	3	4	106	-101
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3	17	3	25	-21	5	21	3	52	50	-1	28	3	24	-16	-4	2	4	44	39	-8	4	4	37	40
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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0	4	4	187	192	0	6	4	129	135	0	8	4	44	46	-1	10	4	84	88	-7	12	4	98	-101
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2	4	4	78	82	2	6	4	185	-185	2	8	4	89	-82	1	10	4	86	-85	-2	12	4	65	66
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5	4	4	28	-27	5	6	4	64	-62	7	8	4	53	-52	5	10	4	91	-98	2	12	4	37	-30
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13	5	4	30	-26	-10	8	4	52	52	-10	10	4	34	-29	8	11	4	75	73	12	13	4	47	-52
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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2	14	4	47	48	5	17	4	37	36	0	22	4	48	45	11	0	5	24	20	9	2	5	30	-26
3	14	4	95	-96	9	17	4	57	51	1	22	4	63	-67	13	0	5	52	58	10	2	5	50	-48
4	14	4	71	68	-6	18	4	33	-39	3	22	4	64	56	-10	1	5	57	-62	11	2	5	33	32
10	14	4	57	-57	-1	18	4	68	74	8	22	4	31	28	-8	1	5	59	57	12	2	5	41	-42
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-1	15	4	23	-19	-1	19	4	33	22	-9	26	4	40	-38	2	1	5	134	129	1	3	5	168	-169
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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6	14	5	49	50	6	17	5	59	-57	-6	22	5	54	-57	-10	0	6	36	-23	-1	2	6	42	-41
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11	14	5	50	42	-11	18	5	23	20	-4	22	5	47	51	-6	0	6	79	83	1	2	6	45	-44
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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0	4	6	67	-67	-2	6	6	33	-32	-10	8	6	49	56	-4	10	6	42	46	11	12	6	40	-38
2	4	6	24	26	-1	6	6	33	37	-8	8	6	75	-77	-2	10	6	50	-45	12	12	6	29	28
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10	4	6	56	-58	3	6	6	37	-35	-3	8	6	120	-105	3	10	6	120	113	-3	13	6	29	30
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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2	6	7	15	-12	0	8	7	104	99	-3	10	7	83	-84	6	12	7	42	40	0	15	7	62	62
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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-1	17	7	44	48	-2	20	7	29	-24	-8	0	8	146	-150	-8	2	8	70	70	-11	4	8	47	46
0	17	7	50	-57	0	20	7	42	-40	-6	0	8	222	226	-7	2	8	92	96	-9	4	8	31	-33
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3	17	7	27	-27	4	20	7	38	-38	-2	0	8	49	40	-5	2	8	45	-41	-4	4	8	93	-90
4	17	7	93	88	9	20	7	25	-20	0	0	8	53	50	-4	2	8	58	-58	-2	4	8	32	-31
5	17	7	69	68	-9	21	7	25	-21	2	0	8	164	-156	-3	2	8	43	-41	-1	4	8	167	-155
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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1	21	8	38	26	5	0	9	114	-105	9	2	9	53	53	-9	5	9	82	78	-1	7	9	84	85
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8	21	8	31	24	-9	1	9	125	127	-12	3	9	42	37	-5	5	9	100	94	1	7	9	57	-55
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-10	22	8	23	19	-5	1	9	26	-28	-6	3	9	44	-47	-3	5	9	149	-146	4	7	9	102	-97

Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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7	7	9	41	41	-9	10	9	43	-41	-4	12	9	87	85	-12	15	9	23	17	4	17	9	110	104
8	7	9	26	20	-6	10	9	97	98	-1	12	9	22	26	-10	15	9	45	-45	5	17	9	28	37
9	7	9	60	-60	-5	10	9	62	63	0	12	9	59	-59	-6	15	9	30	-31	6	17	9	33	-23
14	7	9	33	25	-4	10	9	49	-51	1	12	9	58	53	-4	15	9	65	65	7	17	9	24	-30
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0	8	9	31	-35	7	10	9	46	-50	-8	13	9	59	59	-12	16	9	41	-33	-4	19	9	57	-50
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0	9	9	96	-88	2	11	9	53	56	-5	14	9	23	-29	-11	17	9	24	-18	6	20	9	36	32
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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0	22	9	65	-67	-1	1	10	40	-36	4	3	10	112	-102	7	5	10	19	-12	2	7	10	21	-21
3	22	9	38	-41	0	1	10	68	-68	5	3	10	25	-26	9	5	10	28	-29	-7	8	10	36	-41
-6	23	9	41	-38	1	1	10	126	-121	6	3	10	64	67	10	5	10	31	-34	-3	8	10	76	82
0	23	9	29	-33	2	1	10	25	-25	7	3	10	61	-63	11	5	10	20	20	-2	8	10	34	-36
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10	0	10	74	-83	11	2	10	45	42	-7	5	10	66	68	12	6	10	32	24	9	9	10	28	-29
12	0	10	29	30	14	2	10	35	-32	-5	5	10	42	-48	-12	7	10	37	39	11	9	10	59	59
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-8	1	10	104	-106	-6	3	10	21	-15	0	5	10	69	64	-6	7	10	44	55	-6	10	10	78	-77
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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3	10	10	63	-69	10	12	10	33	-27	10	15	10	32	28	-6	20	10	33	-36	-4	28	10	23	-17
4	10	10	54	-55	-11	13	10	31	28	11	15	10	37	-33	-5	20	10	21	25	-13	0	11	39	36
5	10	10	63	71	-10	13	10	39	43	-9	16	10	31	-33	1	20	10	44	-42	-11	0	11	47	43
6	10	10	59	60	-8	13	10	29	-31	-5	16	10	66	-68	2	20	10	33	-34	-9	0	11	120	-130
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12	10	10	25	-23	-4	13	10	21	25	-2	16	10	70	-68	7	20	10	29	-35	-3	0	11	93	-84
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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0	2	11	148	142	5	4	11	82	-88	-7	7	11	32	35	5	9	11	45	46	-2	12	11	29	32
1	2	11	40	50	7	4	11	50	51	-4	7	11	56	47	7	9	11	32	25	0	12	11	56	-58
2	2	11	116	-121	8	4	11	59	-54	-3	7	11	113	-114	8	9	11	24	-8	2	12	11	115	108
4	2	11	26	-31	9	4	11	29	-31	-2	7	11	25	29	9	9	11	25	-31	3	12	11	49	48
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9	3	11	53	49	-6	6	11	62	63	5	8	11	25	-26	0	11	11	85	-89	1	14	11	41	38
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Table 2 - continued.

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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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3	14	14	28	27	0	21	14	57	58	4	1	15	46	51	-6	5	15	34	34	0	8	15	33	-37
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0	16	14	69	-68	3	24	14	41	-37	10	2	15	21	-22	-4	6	15	54	60	0	9	15	42	-45
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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2	10	15	68	-67	-3	14	15	23	29	-6	20	15	28	-26	10	1	16	50	54	4	4	16	29	-23
3	10	15	85	88	1	14	15	49	-48	3	20	15	27	-22	-14	2	16	26	19	5	4	16	54	53
4	10	15	34	-33	6	14	15	35	38	1	21	15	21	-18	-8	2	16	28	21	6	4	16	63	-62
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-8	11	15	38	-47	-2	15	15	33	-35	-6	22	15	32	-28	-1	2	16	21	-21	-8	5	16	41	40
-7	11	15	58	-55	-1	15	15	42	-35	-4	22	15	30	25	0	2	16	74	74	-6	5	16	58	-58
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-1	11	15	38	-43	9	15	15	26	-26	-6	24	15	35	22	3	2	16	63	-58	-1	5	16	29	25
0	11	15	32	38	-8	16	15	31	-31	-5	24	15	37	-33	5	2	16	23	33	0	5	16	46	-47
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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2	8	16	99	100	-5	12	16	50	-50	1	17	16	32	37	2	1	17	88	-92	-7	5	17	88	-94
3	8	16	31	-26	-4	12	16	38	-37	4	17	16	31	-27	4	1	17	60	60	-1	5	17	60	68
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H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
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7	8	17	26	-36	4	14	17	39	-48	-10	0	18	46	38	-7	4	18	48	-48	-6	10	18	47	-51
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Table 2 - continued.

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
9	14	18	26	23	7	1	19	31	-31	0	6	19	24	18	2	13	19	50	-53	-5	3	20	29	-31
-6	15	18	47	-45	-9	2	19	25	14	1	6	19	26	-33	3	13	19	25	-16	-4	3	20	41	40
-4	15	18	21	17	-8	2	19	38	-40	4	6	19	40	40	5	13	19	35	39	1	3	20	61	-65
-2	15	18	31	-33	-5	2	19	21	14	-5	7	19	27	24	7	13	19	29	-26	6	3	20	31	27
1	15	18	31	-21	-4	2	19	48	-48	0	7	19	40	-45	-8	14	19	33	-33	-10	4	20	45	44
3	15	18	38	36	-3	2	19	44	-52	2	7	19	34	28	-7	14	19	39	-23	-6	4	20	27	-20
-5	16	18	21	-10	-2	2	19	60	63	3	7	19	35	38	-3	14	19	24	-20	-3	4	20	26	28
8	16	18	26	-30	4	2	19	29	39	8	7	19	23	21	8	14	19	32	35	1	4	20	25	-25
-8	17	18	29	28	5	2	19	25	2	10	7	19	22	20	-9	15	19	31	-24	4	4	20	42	53
-1	17	18	34	-29	6	2	19	28	-36	-6	8	19	38	-35	1	15	19	29	-21	-3	5	20	27	-36
-2	18	18	27	-23	11	2	19	43	-41	-2	8	19	40	-49	0	17	19	31	25	-2	5	20	62	59
0	18	18	25	23	-11	3	19	32	36	-1	8	19	30	27	1	17	19	27	-20	3	5	20	51	-45
1	18	18	39	33	-9	3	19	33	-31	1	8	19	39	35	-5	20	19	25	-21	-11	6	20	23	9
5	18	18	30	25	0	3	19	68	71	2	8	19	42	40	-1	21	19	26	-15	-2	6	20	25	-17
-3	19	18	27	-30	2	3	19	56	49	8	8	19	33	-32	-4	22	19	27	-27	-1	6	20	48	-41
-2	19	18	21	16	3	3	19	22	20	-7	9	19	20	17	-3	23	19	23	16	6	6	20	23	-9
2	20	18	27	-27	5	3	19	58	-55	-4	9	19	48	-43	2	23	19	24	25	-7	7	20	62	-62
-6	21	18	34	33	7	3	19	37	44	-2	9	19	20	21	-12	0	20	25	-4	-2	7	20	33	-31
-1	21	18	28	-25	-7	4	19	35	41	-1	9	19	41	-49	-8	0	20	38	40	1	7	20	60	57
-4	22	18	30	32	-5	4	19	62	-61	0	9	19	35	35	-6	0	20	37	37	-9	8	20	30	34
-3	22	18	29	-16	-3	4	19	63	66	2	9	19	31	-47	-4	0	20	52	60	-1	8	20	44	42
-7	0	19	42	-34	-1	4	19	68	-66	-10	10	19	29	-29	2	0	20	26	-17	2	8	20	38	-38
-3	0	19	140	126	0	4	19	49	53	-5	10	19	59	63	-8	1	20	35	-40	4	8	20	37	34
-1	0	19	50	-44	1	4	19	27	27	-3	10	19	46	-51	-3	1	20	43	39	-8	9	20	25	20
1	0	19	45	-37	2	4	19	52	-58	10	10	19	30	-32	8	1	20	37	29	-6	9	20	30	26
3	0	19	36	36	7	4	19	39	36	-5	11	19	47	-47	-4	2	20	21	-12	-5	9	20	25	-28
7	0	19	39	-35	-11	5	19	31	-21	-4	11	19	45	43	-3	2	20	26	30	-4	9	20	53	-57
-8	1	19	29	-23	-9	5	19	39	39	6	11	19	21	16	0	2	20	37	-36	0	9	20	34	36
-4	1	19	22	25	-7	5	19	67	-71	-8	12	19	37	34	1	2	20	50	45	3	9	20	29	-26
-1	1	19	53	47	1	5	19	45	45	-6	12	19	58	-57	5	2	20	28	-26	6	9	20	32	-31
1	1	19	31	-15	5	5	19	27	19	-4	12	19	46	44	7	2	20	24	32	9	9	20	30	-35
2	1	19	51	-55	-11	6	19	32	27	-3	12	19	35	32	-9	3	20	36	35	-7	10	20	22	-17
4	1	19	24	18	-7	6	19	45	-39	-1	12	19	40	-36	-8	3	20	27	17	-4	10	20	38	-35
5	1	19	43	41	-3	6	19	26	-31	2	12	19	40	-33	-6	3	20	31	-34	-3	10	20	40	-41

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
-2	10	20	33	38	7	2	21	42	-40	-5	9	21	29	-34	-10	2	22	22	-1	-4	10	22	68	-63
2	10	20	27	30	-6	3	21	30	-28	-3	9	21	41	41	-9	2	22	37	-35	0	10	22	27	28
-6	11	20	38	-37	-4	3	21	27	29	-7	10	21	27	-23	-1	2	22	21	-8	-8	11	22	38	25
-5	11	20	52	48	1	3	21	59	-58	-5	10	21	42	45	0	2	22	21	-10	-6	11	22	40	-33
-4	11	20	55	53	2	3	21	35	38	-1	10	21	41	-36	0	3	22	24	-26	-9	12	22	25	21
-3	12	20	20	-4	-11	4	21	24	25	1	10	21	47	46	2	3	22	37	35	-3	12	22	22	-23
1	12	20	34	-31	-1	4	21	39	-36	4	10	21	22	-19	4	3	22	23	-25	-3	13	22	37	-36
3	12	20	31	37	4	4	21	30	33	6	10	21	25	-17	-6	4	22	22	-28	3	13	22	28	25
-5	13	20	28	-27	-7	5	21	22	19	-3	11	21	39	-36	-5	4	22	24	-29	-5	15	22	27	17
7	13	20	29	19	-4	5	21	27	-22	1	11	21	25	19	-2	4	22	26	-16	0	15	22	44	-47
8	13	20	30	29	-3	5	21	21	33	2	11	21	50	48	0	4	22	22	8	0	18	22	28	-25
-4	14	20	37	33	0	5	21	28	32	3	11	21	22	-17	3	4	22	30	29	1	18	22	22	8
0	14	20	44	-51	2	5	21	32	-34	-7	12	21	41	31	-6	5	22	23	-21	-9	0	23	28	-28
3	14	20	50	-47	-7	6	21	24	-20	-5	12	21	41	-37	-7	6	22	43	39	3	0	23	38	39
-6	15	20	34	-34	-6	6	21	32	28	2	12	21	32	19	-2	6	22	49	47	-7	1	23	33	32
-3	15	20	23	11	-3	6	21	37	-40	-8	13	21	27	27	0	6	22	22	-15	-5	1	23	59	-49
6	15	20	34	32	-2	6	21	37	-45	-5	13	21	29	29	2	6	22	52	-54	-2	1	23	29	16
-5	16	20	23	-9	-1	6	21	47	45	-7	14	21	27	-27	-10	7	22	24	-14	-8	2	23	43	44
-1	16	20	26	26	0	6	21	39	45	3	14	21	29	23	-7	7	22	29	-30	-2	2	23	25	-22
0	16	20	31	26	6	6	21	27	-21	6	14	21	24	-27	-3	7	22	47	52	1	2	23	30	33
4	16	20	38	-28	7	6	21	27	31	-1	15	21	32	28	-1	7	22	46	-43	3	2	23	52	-52
-5	17	20	24	-24	-5	7	21	21	17	1	15	21	26	-30	0	7	22	20	10	1	3	23	21	15
-1	18	20	39	-28	-3	7	21	30	-30	2	15	21	24	26	1	7	22	30	27	7	3	23	35	-34
3	19	20	24	22	-2	7	21	47	40	5	15	21	31	32	-7	8	22	33	-35	-5	4	23	22	17
-7	0	21	51	59	-1	7	21	24	18	-7	16	21	28	26	-4	8	22	30	32	-4	4	23	28	30
3	0	21	45	51	0	7	21	39	-39	-6	17	21	25	-25	-1	8	22	43	42	-2	4	23	29	-22
-8	1	21	33	38	4	7	21	34	35	-2	17	21	26	-25	-7	9	22	33	28	1	4	23	31	-27
-2	1	21	36	-54	8	7	21	32	30	1	17	21	27	20	-3	9	22	22	-20	2	4	23	22	19
-1	1	21	21	-19	-8	8	21	29	28	0	18	21	27	28	-2	9	22	28	-27	1	5	23	34	-33
0	1	21	24	18	-3	8	21	26	24	2	18	21	24	17	4	9	22	30	32	3	5	23	35	26
1	1	21	29	21	3	8	21	40	38	-8	0	22	42	45	5	9	22	22	-23	-8	6	23	34	-35
9	1	21	24	-20	4	8	21	21	-23	-6	1	22	51	47	6	9	22	37	-38	-6	6	23	28	-18
-1	2	21	27	-26	5	8	21	36	-38	-2	1	22	27	-27	-7	10	22	23	-24	-1	6	23	31	-39
3	2	21	41	-44	-8	9	21	23	-23	2	1	22	26	-39	-6	10	22	27	23	0	6	23	42	37

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
3	6	23	29	17	-2	14	23	33	-31	-7	6	24	27	18	6	2	25	35	-31	2	2	26	37	-40
-8	7	23	35	-33	1	15	23	33	30	-5	7	24	34	-34	1	3	25	45	46	-4	4	26	27	-24
-1	7	23	41	36	-1	17	23	30	-26	0	7	24	45	-42	2	3	25	24	-18	-1	4	26	23	26
-8	8	23	41	35	0	17	23	29	-25	-7	8	24	28	-25	-1	5	25	49	45	0	4	26	33	-29
-2	8	23	35	39	-4	0	24	33	39	-1	9	24	27	14	1	5	25	27	-29	3	4	26	23	-23
0	8	23	35	-30	-2	0	24	43	35	-2	10	24	25	-31	-1	6	25	32	-24	-6	5	26	32	-29
3	8	23	33	31	2	1	24	39	-40	-4	11	24	27	-27	3	6	25	24	25	-3	5	26	27	-22
6	8	23	28	25	3	1	24	27	-22	-3	11	24	37	36	-1	7	25	29	-36	-2	6	26	26	-24
-9	9	23	28	-22	-4	2	24	31	-24	2	11	24	22	1	1	7	25	28	27	0	6	26	48	47
-8	10	23	26	-31	1	2	24	27	-21	5	11	24	24	-22	4	7	25	23	22	-2	7	26	25	-7
-3	10	23	47	47	7	2	24	34	-28	-3	13	24	47	-42	-6	8	25	30	18	1	7	26	27	-11
-7	11	23	27	-24	-6	3	24	25	19	-1	13	24	37	33	0	8	25	28	-12	-2	8	26	24	11
-5	11	23	32	33	2	3	24	34	29	0	14	24	28	23	-3	9	25	25	-9	1	0	27	24	-14
1	11	23	30	-6	-7	4	24	23	18	-2	16	24	24	-25	4	9	25	25	-29	2	2	27	24	-11
4	11	23	21	10	0	4	24	48	-39	1	0	25	30	-35	1	11	25	28	-22	-3	6	27	24	-16
-7	12	23	25	14	2	4	24	32	24	-2	1	25	34	29	-5	1	26	24	21	-1	6	27	24	27
4	13	23	32	-33	0	5	24	26	30	1	2	25	26	18	4	1	26	32	-32	-2	8	27	23	10
5	13	23	24	-15	2	5	24	38	36	2	2	25	27	24										

Table 3 - Bond lengths (Å) with estimated standard deviations in parentheses for the least significant figure.

TI(1)	- O(1)	1.793(5)	C(37)	- C(42)	1.41 (1)
TI(1)	- O(5)	1.780(6)	C(38)	- C(39)	1.40 (2)
TI(1)	- O(6)	1.777(6)	C(39)	- C(40)	1.34 (2)
TI(1)	- O(10)	1.788(7)	C(40)	- C(41)	1.39 (2)
O(1)	- SI(1)	1.628(6)	C(41)	- C(42)	1.40 (2)
SI(1)	- C(1)	1.852(9)	C(43)	- C(44)	1.39 (2)
SI(1)	- C(7)	1.84 (1)	C(43)	- C(48)	1.40 (1)
SI(1)	- O(2)	1.613(6)	C(44)	- C(45)	1.42 (2)
C(1)	- C(2)	1.35 (1)	C(45)	- C(46)	1.37 (2)
C(1)	- C(6)	1.39 (1)	C(46)	- C(47)	1.33 (2)
C(2)	- C(3)	1.39 (2)	C(47)	- C(48)	1.41 (2)
C(3)	- C(4)	1.37 (2)	O(6)	- SI(5)	1.629(6)
C(4)	- C(5)	1.35 (2)	SI(5)	- C(49)	1.84 (1)
C(5)	- C(6)	1.41 (2)	SI(5)	- C(55)	1.85 (1)
C(7)	- C(8)	1.41 (2)	SI(5)	- O(7)	1.613(6)
C(7)	- C(12)	1.40 (2)	C(49)	- C(50)	1.38 (1)
C(8)	- C(9)	1.40 (2)	C(49)	- C(54)	1.36 (1)
C(9)	- C(10)	1.35 (2)	C(50)	- C(51)	1.42 (2)
C(10)	- C(11)	1.38 (2)	C(51)	- C(52)	1.37 (2)
C(11)	- C(12)	1.41 (2)	C(52)	- C(53)	1.37 (2)
O(2)	- SI(2)	1.611(6)	C(53)	- C(54)	1.41 (2)
SI(2)	- C(13)	1.86 (1)	C(55)	- C(56)	1.39 (2)
SI(2)	- C(19)	1.837(9)	C(55)	- C(60)	1.35 (2)
SI(2)	- O(3)	1.608(7)	C(56)	- C(57)	1.43 (2)
C(13)	- C(14)	1.37 (1)	C(57)	- C(58)	1.31 (2)
C(13)	- C(18)	1.39 (2)	C(58)	- C(59)	1.35 (2)
C(14)	- C(15)	1.42 (2)	C(59)	- C(60)	1.45 (2)
C(15)	- C(16)	1.33 (2)	O(7)	- SI(6)	1.611(6)
C(16)	- C(17)	1.32 (2)	SI(6)	- C(61)	1.87 (1)
C(17)	- C(18)	1.42 (2)	SI(6)	- C(67)	1.83 (1)
C(19)	- C(20)	1.38 (1)	SI(6)	- O(8)	1.620(7)
C(19)	- C(24)	1.38 (1)	C(61)	- C(62)	1.37 (2)
C(20)	- C(21)	1.40 (2)	C(61)	- C(66)	1.39 (2)
C(21)	- C(22)	1.36 (2)	C(62)	- C(63)	1.46 (2)
C(22)	- C(23)	1.39 (2)	C(63)	- C(64)	1.33 (2)
C(23)	- C(24)	1.42 (2)	C(64)	- C(65)	1.33 (2)
O(3)	- SI(3)	1.607(7)	C(65)	- C(66)	1.44 (2)
SI(3)	- C(25)	1.86 (1)	C(67)	- C(68)	1.41 (2)
SI(3)	- C(31)	1.85 (1)	C(67)	- C(72)	1.38 (2)
SI(3)	- O(4)	1.616(7)	C(68)	- C(69)	1.39 (2)
C(25)	- C(26)	1.37 (2)	C(69)	- C(70)	1.31 (2)
C(25)	- C(30)	1.41 (2)	C(70)	- C(71)	1.37 (2)
C(26)	- C(27)	1.47 (2)	C(71)	- C(72)	1.44 (2)
C(27)	- C(28)	1.34 (2)	O(8)	- SI(7)	1.61 (6)
C(28)	- C(29)	1.35 (2)	SI(7)	- C(73)	1.854(9)
C(29)	- C(30)	1.46 (2)	SI(7)	- C(79)	1.858(9)
C(31)	- C(32)	1.34 (2)	SI(7)	- O(9)	1.620(7)
C(31)	- C(36)	1.43 (2)	C(73)	- C(74)	1.40 (1)
C(32)	- C(33)	1.46 (2)	C(73)	- C(78)	1.38 (1)
C(33)	- C(34)	1.34 (2)	C(74)	- C(75)	1.42 (2)
C(34)	- C(35)	1.37 (2)	C(75)	- C(76)	1.34 (2)
C(35)	- C(36)	1.47 (2)	C(76)	- C(77)	1.35 (2)
O(4)	- SI(4)	1.608(6)	C(77)	- C(78)	1.40 (2)
SI(4)	- C(37)	1.853(9)	C(79)	- C(80)	1.39 (1)
SI(4)	- C(43)	1.84 (1)	C(79)	- C(84)	1.39 (1)
SI(4)	- O(5)	1.628(6)	C(80)	- C(81)	1.42 (2)
C(37)	- C(38)	1.38 (1)	C(81)	- C(82)	1.34 (2)

Table 3 - Continued

C(82)	- C(83)	1.38 (2)
C(83)	- C(84)	1.38 (2)
O(9)	- SI(8)	1.608(6)
SI(8)	- C(85)	1.853(9)
SI(8)	- C(91)	1.835(9)
SI(8)	- O(10)	1.614(7)
C(85)	- C(86)	1.37 (1)
C(85)	- C(90)	1.38 (1)
C(86)	- C(87)	1.42 (2)
C(87)	- C(88)	1.37 (2)
C(88)	- C(89)	1.34 (2)
C(89)	- C(90)	1.41 (2)
C(91)	- C(92)	1.38 (2)
C(91)	- C(96)	1.35 (2)
C(92)	- C(93)	1.41 (2)
C(93)	- C(94)	1.34 (2)
C(94)	- C(95)	1.36 (2)
C(95)	- C(96)	1.43 (2)

Table 4 - Bond angles (degrees) with estimated standard deviations in parentheses for the least significant figure.

O(6)	- TI(1) -	O(10)	107.7(3)	C(25)	- SI(3) -	O(4)	108.2(5)
O(5)	- TI(1) -	O(10)	108.9(3)	C(25)	- SI(3) -	C(31)	112.6(5)
O(5)	- TI(1) -	O(6)	109.4(3)	SI(3)	- C(25) -	C(30)	118.3(9)
O(1)	- TI(1) -	O(10)	109.7(3)	SI(3)	- C(25) -	C(26)	120.9(9)
O(1)	- TI(1) -	O(6)	110.7(3)	C(26)	- C(25) -	C(30)	121 (1)
O(1)	- TI(1) -	O(5)	110.5(3)	C(25)	- C(26) -	C(27)	121 (1)
TI(1)	- O(1) -	SI(1)	162.1(4)	C(26)	- C(27) -	C(28)	114 (1)
O(1)	- SI(1) -	O(2)	109.2(3)	C(27)	- C(28) -	C(29)	131 (1)
O(1)	- SI(1) -	C(7)	110.7(4)	C(28)	- C(29) -	C(30)	114 (1)
O(1)	- SI(1) -	C(1)	108.3(4)	C(25)	- C(30) -	C(29)	120 (1)
C(7)	- SI(1) -	O(2)	108.2(4)	SI(3)	- C(31) -	C(36)	117.9(9)
C(1)	- SI(1) -	O(2)	109.5(4)	SI(3)	- C(31) -	C(32)	122.2(9)
C(1)	- SI(1) -	C(7)	110.9(4)	C(32)	- C(31) -	C(36)	119 (1)
SI(1)	- C(1) -	C(6)	118.5(7)	C(31)	- C(32) -	C(33)	124 (1)
SI(1)	- C(1) -	C(2)	123.4(7)	C(32)	- C(33) -	C(34)	115 (1)
C(2)	- C(1) -	C(6)	118.1(9)	C(33)	- C(34) -	C(35)	125 (1)
C(1)	- C(2) -	C(3)	122.4(9)	C(34)	- C(35) -	C(36)	118 (1)
C(2)	- C(3) -	C(4)	119 (1)	C(31)	- C(36) -	C(35)	117 (1)
C(3)	- C(4) -	C(5)	121 (1)	SI(3)	- O(4) -	SI(4)	150.1(5)
C(4)	- C(5) -	C(6)	119 (1)	O(4)	- SI(4) -	O(5)	110.6(4)
C(1)	- C(6) -	C(5)	121 (1)	O(4)	- SI(4) -	C(43)	106.6(4)
SI(1)	- C(7) -	C(12)	119.4(8)	O(4)	- SI(4) -	C(37)	110.2(4)
SI(1)	- C(7) -	C(8)	121.6(8)	C(43)	- SI(4) -	O(5)	108.9(4)
C(8)	- C(7) -	C(12)	118.8(9)	C(37)	- SI(4) -	O(5)	106.5(4)
C(7)	- C(8) -	C(9)	120 (1)	C(37)	- SI(4) -	C(43)	114.1(4)
C(8)	- C(9) -	C(10)	120 (1)	SI(4)	- C(37) -	C(42)	120.2(7)
C(9)	- C(10) -	C(11)	123 (1)	SI(4)	- C(37) -	C(38)	121.5(7)
C(10)	- C(11) -	C(12)	118 (1)	C(38)	- C(37) -	C(42)	118.2(9)
C(7)	- C(12) -	C(11)	121 (1)	C(37)	- C(38) -	C(39)	121 (1)
SI(1)	- O(2) -	SI(2)	147.6(4)	C(38)	- C(39) -	C(40)	121 (1)
O(2)	- SI(2) -	O(3)	109.6(4)	C(39)	- C(40) -	C(41)	120 (1)
O(2)	- SI(2) -	C(19)	111.6(4)	C(40)	- C(41) -	C(42)	121 (1)
O(2)	- SI(2) -	C(13)	107.2(4)	C(37)	- C(42) -	C(41)	120 (1)
C(19)	- SI(2) -	O(3)	107.2(4)	SI(4)	- C(43) -	C(48)	121.4(8)
C(13)	- SI(2) -	O(3)	109.1(4)	SI(4)	- C(43) -	C(44)	121.0(8)
C(13)	- SI(2) -	C(19)	112.1(4)	C(44)	- C(43) -	C(48)	117.5(9)
SI(2)	- C(13) -	C(18)	120.0(8)	C(43)	- C(44) -	C(45)	120 (1)
SI(2)	- C(13) -	C(14)	121.3(8)	C(44)	- C(45) -	C(46)	119 (1)
C(14)	- C(13) -	C(18)	119 (1)	C(45)	- C(46) -	C(47)	122 (1)
C(13)	- C(14) -	C(15)	119 (1)	C(46)	- C(47) -	C(48)	119 (1)
C(14)	- C(15) -	C(16)	120 (1)	C(43)	- C(48) -	C(47)	122 (1)
C(15)	- C(16) -	C(17)	124 (1)	TI(1)	- O(5) -	SI(4)	174.2(4)
C(16)	- C(17) -	C(18)	117 (1)	TI(1)	- O(6) -	SI(5)	156.6(4)
C(13)	- C(18) -	C(17)	121 (1)	O(6)	- SI(5) -	O(7)	107.3(4)
SI(2)	- C(19) -	C(24)	119.5(7)	O(6)	- SI(5) -	C(55)	110.7(4)
SI(2)	- C(19) -	C(20)	123.2(7)	O(6)	- SI(5) -	C(49)	107.3(4)
C(20)	- C(19) -	C(24)	117.2(9)	C(55)	- SI(5) -	O(7)	108.3(4)
C(19)	- C(20) -	C(21)	122.6(9)	C(49)	- SI(5) -	O(7)	112.0(4)
C(20)	- C(21) -	C(22)	120 (1)	C(49)	- SI(5) -	C(55)	111.2(4)
C(21)	- C(22) -	C(23)	120 (1)	SI(5)	- C(49) -	C(54)	121.8(7)
C(22)	- C(23) -	C(24)	120 (1)	SI(5)	- C(49) -	C(50)	119.1(8)
C(19)	- C(24) -	C(23)	121 (1)	C(50)	- C(49) -	C(54)	118.9(9)
SI(2)	- O(3) -	SI(3)	157.8(5)	C(49)	- C(50) -	C(51)	120 (1)
O(3)	- SI(3) -	O(4)	109.3(3)	C(50)	- C(51) -	C(52)	118 (1)
O(3)	- SI(3) -	C(31)	108.9(4)	C(51)	- C(52) -	C(53)	123 (1)
O(3)	- SI(3) -	C(25)	109.1(4)	C(52)	- C(53) -	C(54)	117 (1)
C(31)	- SI(3) -	O(4)	108.7(5)	C(49)	- C(54) -	C(53)	123 (1)

Table 4 - Continued.

SI(5)	C(55)	C(60)	120.5(8)	C(85)	SI(8)	C(91)	114.4(4)
SI(5)	C(55)	C(56)	121.1(8)	SI(8)	C(85)	C(90)	121.7(7)
C(56)	C(55)	C(60)	118 (1)	SI(8)	C(85)	C(86)	120.3(7)
C(55)	C(56)	C(57)	120 (1)	C(86)	C(85)	C(90)	117.9(9)
C(56)	C(57)	C(58)	119 (1)	C(85)	C(86)	C(87)	122 (1)
C(57)	C(58)	C(59)	124 (1)	C(86)	C(87)	C(88)	119 (1)
C(58)	C(59)	C(60)	117 (1)	C(87)	C(88)	C(89)	120 (1)
C(55)	C(60)	C(59)	122 (1)	C(88)	C(89)	C(90)	121 (1)
SI(5)	O(7)	SI(6)	172.0(5)	C(85)	C(90)	C(89)	120.4(9)
O(7)	SI(6)	O(8)	108.9(3)	SI(8)	C(91)	C(96)	120.8(9)
O(7)	SI(6)	C(67)	109.3(4)	SI(8)	C(91)	C(92)	124.2(8)
O(7)	SI(6)	C(61)	111.0(4)	C(92)	C(91)	C(96)	115 (1)
C(67)	SI(6)	O(8)	110.5(4)	C(91)	C(92)	C(93)	122 (1)
C(61)	SI(6)	O(8)	105.4(4)	C(92)	C(93)	C(94)	120 (1)
C(61)	SI(6)	C(67)	111.7(5)	C(93)	C(94)	C(95)	120 (1)
SI(6)	C(61)	C(66)	120.4(8)	C(94)	C(95)	C(96)	118 (1)
SI(6)	C(61)	C(62)	118.5(8)	C(91)	C(96)	C(95)	124 (1)
C(62)	C(61)	C(66)	121 (1)	TI(1)	O(10)	SI(8)	172.5(5)
C(61)	C(62)	C(63)	119 (1)				
C(62)	C(63)	C(64)	117 (1)				
C(63)	C(64)	C(65)	126 (1)				
C(64)	C(65)	C(66)	118 (1)				
C(61)	C(66)	C(65)	119 (1)				
SI(6)	C(67)	C(72)	123.2(9)				
SI(6)	C(67)	C(68)	121.1(8)				
C(68)	C(67)	C(72)	116 (1)				
C(67)	C(68)	C(69)	122 (1)				
C(68)	C(69)	C(70)	121 (1)				
C(69)	C(70)	C(71)	122 (1)				
C(70)	C(71)	C(72)	118 (1)				
C(67)	C(72)	C(71)	122 (1)				
SI(6)	O(8)	SI(7)	161.2(5)				
O(8)	SI(7)	O(9)	108.7(4)				
O(8)	SI(7)	C(79)	111.6(4)				
O(8)	SI(7)	C(73)	108.1(4)				
C(79)	SI(7)	O(9)	108.6(4)				
C(73)	SI(7)	O(9)	108.4(4)				
C(73)	SI(7)	C(79)	111.4(4)				
SI(7)	C(73)	C(78)	125.9(7)				
SI(7)	C(73)	C(74)	117.1(7)				
C(74)	C(73)	C(78)	116.9(9)				
C(73)	C(74)	C(75)	120 (1)				
C(74)	C(75)	C(76)	120 (1)				
C(75)	C(76)	C(77)	122 (1)				
C(76)	C(77)	C(78)	119 (1)				
C(73)	C(78)	C(77)	123 (1)				
SI(7)	C(79)	C(84)	119.6(7)				
SI(7)	C(79)	C(80)	122.0(8)				
C(80)	C(79)	C(84)	118.3(9)				
C(79)	C(80)	C(81)	121 (1)				
C(80)	C(81)	C(82)	118 (1)				
C(81)	C(82)	C(83)	123 (1)				
C(82)	C(83)	C(84)	118 (1)				
C(79)	C(84)	C(83)	121 (1)				
SI(7)	O(9)	SI(8)	145.0(5)				
O(9)	SI(8)	O(10)	110.4(4)				
O(9)	SI(8)	C(91)	109.6(4)				
O(9)	SI(8)	C(85)	107.1(4)				
C(91)	SI(8)	O(10)	107.1(4)				
C(85)	SI(8)	O(10)	108.2(4)				

Table 5 - The dihedral angles around the titanium and silicon atoms for hexadeca-phenyloctasiloxyspiro(9,9)titanium(IV).

Plane	**Plane**	**Angle (e.s.d.) in degrees**
O(1)-Ti(1)-O(5)	O(6)-Ti(1)-O(10)	89.8(2)
C(1)-Si(1)-C(7)	O(1)-Si(1)-O(2)	91.3(4)
C(13)-Si(2)-C(19)	O(2)-Si(2)-O(3)	92.2(3)
C(25)-Si(3)-C(31)	O(3)-Si(3)-O(4)	89.7(4)
C(37)-Si(4)-C(43)	O(4)-Si(4)-O(5)	88.0(4)
C(49)-Si(5)-C(55)	O(6)-Si(5)-O(7)	92.5(4)
C(61)-Si(6)-C(67)	O(7)-Si(6)-O(8)	87.5(3)
C(73)-Si(7)-C(79)	O(8)-Si(7)-O(9)	91.1(3)
C(85)-Si(8)-C(91)	O(9)-Si(8)-O(10)	91.2(3)

Table 6 - Torsion angles (degrees) with estimated standard deviations in parentheses for the least significant figure.

O(5)	- TI(1) -	O(6)	- SI(5)	168.7(9)
O(1)	- TI(1) -	O(6)	- SI(5)	-69 (1)
O(5)	- TI(1) -	O(1)	- SI(1)	-33 (1)
O(6)	- TI(1) -	O(1)	- SI(1)	-155 (1)
O(10)	- TI(1) -	O(1)	- SI(1)	87 (1)
O(10)	- TI(1) -	O(6)	- SI(5)	51 (1)
TI(1)	- O(1) -	SI(1)	- C(1)	-64 (1)
TI(1)	- O(1) -	SI(1)	- C(7)	175 (1)
TI(1)	- O(1) -	SI(1)	- O(2)	56 (1)
O(1)	- SI(1) -	O(2)	- SI(2)	37.8(9)
O(1)	- SI(1) -	C(7)	- C(8)	-143.1(8)
O(1)	- SI(1) -	C(7)	- C(12)	41.6(9)
O(1)	- SI(1) -	C(1)	- C(2)	10.3(9)
O(1)	- SI(1) -	C(1)	- C(6)	-168.3(8)
C(7)	- SI(1) -	O(2)	- SI(2)	-82.8(9)
C(1)	- SI(1) -	O(2)	- SI(2)	156.1(8)
C(1)	- SI(1) -	C(7)	- C(8)	96.7(9)
C(1)	- SI(1) -	C(7)	- C(12)	-78.7(9)
C(7)	- SI(1) -	C(1)	- C(6)	-46.6(9)
C(7)	- SI(1) -	C(1)	- C(2)	132.0(8)
O(2)	- SI(1) -	C(1)	- C(6)	72.8(9)
O(2)	- SI(1) -	C(1)	- C(2)	-108.7(8)
O(2)	- SI(1) -	C(7)	- C(12)	161.2(8)
O(2)	- SI(1) -	C(7)	- C(8)	-23 (1)
SI(1)	- C(1) -	C(6)	- C(5)	178.7(9)
SI(1)	- C(1) -	C(2)	- C(3)	-177.3(8)
C(2)	- C(1) -	C(6)	- C(5)	0 (2)
C(6)	- C(1) -	C(2)	- C(3)	1 (1)
C(1)	- C(2) -	C(3)	- C(4)	-3 (2)
C(2)	- C(3) -	C(4)	- C(5)	4 (2)
C(3)	- C(4) -	C(5)	- C(6)	-2 (2)
C(4)	- C(5) -	C(6)	- C(1)	0 (2)
SI(1)	- C(7) -	C(12)	- C(11)	176.3(9)
SI(1)	- C(7) -	C(8)	- C(9)	-174.5(9)
C(8)	- C(7) -	C(12)	- C(11)	1 (2)
C(12)	- C(7) -	C(8)	- C(9)	1 (2)
C(7)	- C(8) -	C(9)	- C(10)	-3 (2)
C(8)	- C(9) -	C(10)	- C(11)	3 (2)
C(9)	- C(10) -	C(11)	- C(12)	-2 (2)
C(10)	- C(11) -	C(12)	- C(7)	-1 (2)
SI(1)	- O(2) -	SI(2)	- C(13)	145.0(8)
SI(1)	- O(2) -	SI(2)	- C(19)	22 (1)
SI(1)	- O(2) -	SI(2)	- O(3)	-96.6(9)
O(2)	- SI(2) -	O(3)	- SI(3)	-40 (1)
O(2)	- SI(2) -	C(19)	- C(20)	80.5(9)
O(2)	- SI(2) -	C(19)	- C(24)	-100.5(8)
O(2)	- SI(2) -	C(13)	- C(14)	16 (1)
O(2)	- SI(2) -	C(13)	- C(18)	-166.7(8)
C(19)	- SI(2) -	O(3)	- SI(3)	-161 (1)
C(13)	- SI(2) -	O(3)	- SI(3)	77 (1)
C(13)	- SI(2) -	C(19)	- C(20)	-40 (1)
C(13)	- SI(2) -	C(19)	- C(24)	139.2(8)
C(19)	- SI(2) -	C(13)	- C(18)	-44 (1)
C(19)	- SI(2) -	C(13)	- C(14)	139.0(9)
O(3)	- SI(2) -	C(13)	- C(18)	75 (1)
O(3)	- SI(2) -	C(13)	- C(14)	-102.5(9)
O(3)	- SI(2) -	C(19)	- C(24)	19.5(9)
O(3)	- SI(2) -	C(19)	- C(20)	-159.5(8)

Table 6 - Continued.

SI(2) - C(13) - C(18) - C(17)	-178	(1)
SI(2) - C(13) - C(14) - C(15)	178.4	(9)
C(14) - C(13) - C(18) - C(17)	-1	(2)
C(18) - C(13) - C(14) - C(15)	1	(2)
C(13) - C(14) - C(15) - C(16)	-2	(2)
C(14) - C(15) - C(16) - C(17)	2	(2)
C(15) - C(16) - C(17) - C(18)	-2	(2)
C(16) - C(17) - C(18) - C(13)	1	(2)
SI(2) - C(19) - C(24) - C(23)	-179.7	(8)
SI(2) - C(19) - C(20) - C(21)	177.2	(8)
C(20) - C(19) - C(24) - C(23)	-1	(1)
C(24) - C(19) - C(20) - C(21)	-2	(1)
C(19) - C(20) - C(21) - C(22)	4	(2)
C(20) - C(21) - C(22) - C(23)	-3	(2)
C(21) - C(22) - C(23) - C(24)	0	(2)
C(22) - C(23) - C(24) - C(19)	2	(2)
SI(2) - O(3) - SI(3) - C(25)	-122	(1)
SI(2) - O(3) - SI(3) - C(31)	1	(1)
SI(2) - O(3) - SI(3) - O(4)	120	(1)
O(3) - SI(3) - O(4) - SI(4)	-11	(1)
O(3) - SI(3) - C(31) - C(32)	83	(1)
O(3) - SI(3) - C(31) - C(36)	-107	(1)
O(3) - SI(3) - C(25) - C(26)	36	(1)
O(3) - SI(3) - C(25) - C(30)	-144.4	(9)
C(31) - SI(3) - O(4) - SI(4)	108.0	(9)
C(25) - SI(3) - O(4) - SI(4)	-129.5	(9)
C(25) - SI(3) - C(31) - C(32)	-156	(1)
C(25) - SI(3) - C(31) - C(36)	15	(1)
C(31) - SI(3) - C(25) - C(30)	95	(1)
C(31) - SI(3) - C(25) - C(26)	-85	(1)
O(4) - SI(3) - C(25) - C(30)	-26	(1)
O(4) - SI(3) - C(25) - C(26)	155	(1)
O(4) - SI(3) - C(31) - C(36)	134.4	(9)
O(4) - SI(3) - C(31) - C(32)	-36	(1)
SI(3) - C(25) - C(30) - C(29)	-179	(1)
SI(3) - C(25) - C(26) - C(27)	177	(1)
C(26) - C(25) - C(30) - C(29)	0	(2)
C(30) - C(25) - C(26) - C(27)	-3	(2)
C(25) - C(26) - C(27) - C(28)	2	(2)
C(26) - C(27) - C(28) - C(29)	1	(3)
C(27) - C(28) - C(29) - C(30)	-3	(2)
C(28) - C(29) - C(30) - C(25)	2	(2)
SI(3) - C(31) - C(36) - C(35)	179	(1)
SI(3) - C(31) - C(32) - C(33)	-178	(1)
C(32) - C(31) - C(36) - C(35)	-11	(2)
C(36) - C(31) - C(32) - C(33)	12	(2)
C(31) - C(32) - C(33) - C(34)	0	(2)
C(32) - C(33) - C(34) - C(35)	-13	(2)
C(33) - C(34) - C(35) - C(36)	14	(2)
C(34) - C(35) - C(36) - C(31)	-1	(2)
SI(3) - O(4) - SI(4) - C(37)	82	(1)
SI(3) - O(4) - SI(4) - C(43)	-153.3	(9)
SI(3) - O(4) - SI(4) - O(5)	-35	(1)
O(4) - SI(4) - C(43) - C(44)	-177.2	(8)
O(4) - SI(4) - C(43) - C(48)	8.0	(9)
O(4) - SI(4) - C(37) - C(38)	-155.0	(8)
O(4) - SI(4) - C(37) - C(42)	26.0	(9)
O(4) - SI(4) - O(5) - TI(1)	-177	(3)
C(37) - SI(4) - C(43) - C(44)	-55	(1)
C(37) - SI(4) - C(43) - C(48)	129.9	(8)
C(43) - SI(4) - C(37) - C(42)	-93.9	(8)

Table 6 - Continued.

C(43) - SI(4) - C(37) - C(38)	85.0(9)	
O(5) - SI(4) - C(37) - C(42)	146.0(8)	
O(5) - SI(4) - C(37) - C(38)	-35.1(9)	
O(5) - SI(4) - C(43) - C(48)	-111.3(8)	
O(5) - SI(4) - C(43) - C(44)	63.5(9)	
SI(4) - C(37) - C(42) - C(41)	179.7(9)	
SI(4) - C(37) - C(38) - C(39)	-179.6(8)	
C(38) - C(37) - C(42) - C(41)	1	(1)
C(42) - C(37) - C(38) - C(39)	-1	(1)
C(37) - C(38) - C(39) - C(40)	1	(2)
C(38) - C(39) - C(40) - C(41)	-1	(2)
C(39) - C(40) - C(41) - C(42)	1	(2)
C(40) - C(41) - C(42) - C(37)	-1	(2)
SI(4) - O(5) - TI(1) - O(1)	-169	(3)
SI(4) - C(43) - C(48) - C(47)	175.2(8)	
SI(4) - C(43) - C(44) - C(45)	-176.0(9)	
C(44) - C(43) - C(48) - C(47)	0	(2)
C(48) - C(43) - C(44) - C(45)	-1	(2)
C(43) - C(44) - C(45) - C(46)	1	(2)
C(44) - C(45) - C(46) - C(47)	-1	(2)
C(45) - C(46) - C(47) - C(48)	0	(2)
C(46) - C(47) - C(48) - C(43)	0	(2)
TI(1) - O(6) - SI(5) - C(49)	92	(1)
TI(1) - O(6) - SI(5) - C(55)	-147.0(9)	
TI(1) - O(6) - SI(5) - O(7)	-29	(1)
O(6) - SI(5) - C(55) - C(56)	-87.5(9)	
O(6) - SI(5) - C(55) - C(60)	91.8(9)	
O(6) - SI(5) - C(49) - C(50)	162.5(8)	
O(6) - SI(5) - C(49) - C(54)	-22.8(9)	
O(6) - SI(5) - O(7) - SI(6)	162	(2)
C(49) - SI(5) - C(55) - C(56)	32	(1)
C(49) - SI(5) - C(55) - C(60)	-149.1(9)	
C(55) - SI(5) - C(49) - C(54)	-144.0(8)	
C(55) - SI(5) - C(49) - C(50)	41.3(9)	
O(7) - SI(5) - C(49) - C(54)	94.7(8)	
O(7) - SI(5) - C(49) - C(50)	-80.1(9)	
O(7) - SI(5) - C(55) - C(60)	-26	(1)
O(7) - SI(5) - C(55) - C(56)	155.1(8)	
SI(5) - C(49) - C(54) - C(53)	-176.0(8)	
SI(5) - C(49) - C(50) - C(51)	175.1(8)	
C(50) - C(49) - C(54) - C(53)	-1	(2)
C(54) - C(49) - C(50) - C(51)	0	(2)
C(49) - C(50) - C(51) - C(52)	2	(2)
C(50) - C(51) - C(52) - C(53)	-2	(2)
C(51) - C(52) - C(53) - C(54)	1	(2)
C(52) - C(53) - C(54) - C(49)	1	(2)
SI(5) - C(55) - C(60) - C(59)	179.6(9)	
SI(5) - C(55) - C(56) - C(57)	-178.4(9)	
SI(5) - O(7) - SI(6) - O(8)	-160	(2)
C(56) - C(55) - C(60) - C(59)	-1	(2)
C(60) - C(55) - C(56) - C(57)	2	(2)
C(55) - C(56) - C(57) - C(58)	-3	(2)
C(56) - C(57) - C(58) - C(59)	3	(2)
C(57) - C(58) - C(59) - C(60)	-2	(2)
C(58) - C(59) - C(60) - C(55)	1	(2)
O(7) - SI(6) - O(8) - SI(7)	87	(1)
O(7) - SI(6) - C(67) - C(68)	174.3(8)	
O(7) - SI(6) - C(67) - C(72)	-12	(1)
O(7) - SI(6) - C(61) - C(62)	-75	(1)
O(7) - SI(6) - C(61) - C(66)	104.9(9)	
C(67) - SI(6) - O(8) - SI(7)	-33	(2)

Table 6 - Continued.

C(61) - SI(6) - O(8) - SI(7)	-154	(1)
C(61) - SI(6) - C(67) - C(68)	51	(1)
C(61) - SI(6) - C(67) - C(72)	-135.3	(9)
C(67) - SI(6) - C(61) - C(66)	-132.9	(9)
C(67) - SI(6) - C(61) - C(62)	48	(1)
O(8) - SI(6) - C(61) - C(66)	-13	(1)
O(8) - SI(6) - C(61) - C(62)	167.8	(9)
O(8) - SI(6) - C(67) - C(72)	107.7	(9)
O(8) - SI(6) - C(67) - C(68)	-65.9	(9)
SI(6) - C(61) - C(66) - C(65)	178.3	(9)
SI(6) - C(61) - C(62) - C(63)	-179	(1)
C(62) - C(61) - C(66) - C(65)	-2	(2)
C(66) - C(61) - C(62) - C(63)	2	(2)
C(61) - C(62) - C(63) - C(64)	2	(2)
C(62) - C(63) - C(64) - C(65)	-6	(2)
C(63) - C(64) - C(65) - C(66)	5	(2)
C(64) - C(65) - C(66) - C(61)	-1	(2)
SI(6) - C(67) - C(72) - C(71)	-178.6	(9)
SI(6) - C(67) - C(68) - C(69)	176.4	(9)
C(68) - C(67) - C(72) - C(71)	-5	(2)
C(72) - C(67) - C(68) - C(69)	2	(2)
C(67) - C(68) - C(69) - C(70)	1	(2)
C(68) - C(69) - C(70) - C(71)	-3	(2)
C(69) - C(70) - C(71) - C(72)	0	(2)
C(70) - C(71) - C(72) - C(67)	3	(2)
SI(6) - O(8) - SI(7) - C(73)	117	(1)
SI(6) - O(8) - SI(7) - C(79)	-6	(2)
SI(6) - O(8) - SI(7) - O(9)	-126	(1)
O(8) - SI(7) - O(9) - SI(8)	19.0	(9)
O(8) - SI(7) - C(79) - C(80)	-130.7	(8)
O(8) - SI(7) - C(79) - C(84)	51.8	(9)
O(8) - SI(7) - C(73) - C(74)	176.3	(7)
O(8) - SI(7) - C(73) - C(78)	-8	(1)
C(79) - SI(7) - O(9) - SI(8)	-102.6	(8)
C(73) - SI(7) - O(9) - SI(8)	136.2	(8)
C(73) - SI(7) - C(79) - C(80)	108.4	(9)
C(73) - SI(7) - C(79) - C(84)	-69.1	(9)
C(79) - SI(7) - C(73) - C(78)	115.0	(9)
C(79) - SI(7) - C(73) - C(74)	-60.7	(9)
O(9) - SI(7) - C(73) - C(78)	-125.6	(8)
O(9) - SI(7) - C(73) - C(74)	58.7	(9)
O(9) - SI(7) - C(79) - C(84)	171.6	(7)
O(9) - SI(7) - C(79) - C(80)	-10.9	(9)
SI(7) - C(73) - C(78) - C(77)	-178.0	(8)
SI(7) - C(73) - C(74) - C(75)	176.0	(9)
C(74) - C(73) - C(78) - C(77)	-2	(1)
C(78) - C(73) - C(74) - C(75)	0	(2)
C(73) - C(74) - C(75) - C(76)	2	(2)
C(74) - C(75) - C(76) - C(77)	-2	(2)
C(75) - C(76) - C(77) - C(78)	0	(2)
C(76) - C(77) - C(78) - C(73)	3	(2)
SI(7) - C(79) - C(84) - C(83)	-179.9	(8)
SI(7) - C(79) - C(80) - C(81)	-179.0	(8)
C(80) - C(79) - C(84) - C(83)	3	(1)
C(84) - C(79) - C(80) - C(81)	-2	(2)
C(79) - C(80) - C(81) - C(82)	0	(2)
C(80) - C(81) - C(82) - C(83)	1	(2)
C(81) - C(82) - C(83) - C(84)	0	(2)
C(82) - C(83) - C(84) - C(79)	-2	(2)
SI(7) - O(9) - SI(8) - C(85)	167.6	(7)
SI(7) - O(9) - SI(8) - C(91)	-67.7	(9)

Table 6 - Continued.

SI(7)	O(9)	SI(8)	O(10)	50.0(9)
O(9)	SI(8)	C(91)	C(92)	115.3(9)
O(9)	SI(8)	C(91)	C(96)	-65 (1)
O(9)	SI(8)	C(85)	C(86)	-157.7(8)
O(9)	SI(8)	C(85)	C(90)	18.6(9)
O(9)	SI(8)	O(10)	TI(1)	-137 (2)
C(85)	SI(8)	C(91)	C(92)	-124.4(9)
C(85)	SI(8)	C(91)	C(96)	55 (1)
C(91)	SI(8)	C(85)	C(90)	-103.0(8)
C(91)	SI(8)	C(85)	C(86)	80.7(9)
O(10)	SI(8)	C(85)	C(90)	137.7(8)
O(10)	SI(8)	C(85)	C(86)	-38.6(9)
O(10)	SI(8)	C(91)	C(96)	175.1(9)
O(10)	SI(8)	C(91)	C(92)	-5 (1)
SI(8)	C(85)	C(90)	C(89)	-178.0(8)
SI(8)	C(85)	C(86)	C(87)	176.8(8)
C(86)	C(85)	C(90)	C(89)	-2 (1)
C(90)	C(85)	C(86)	C(87)	0 (1)
C(85)	C(86)	C(87)	C(88)	1 (2)
C(86)	C(87)	C(88)	C(89)	-1 (2)
C(87)	C(88)	C(89)	C(90)	-1 (2)
C(88)	C(89)	C(90)	C(85)	2 (2)
SI(8)	C(91)	C(96)	C(95)	175 (1)
SI(8)	C(91)	C(92)	C(93)	-179.7(9)
SI(8)	O(10)	TI(1)	O(6)	64 (2)
C(92)	C(91)	C(96)	C(95)	-5 (2)
C(96)	C(91)	C(92)	C(93)	1 (2)
C(91)	C(92)	C(93)	C(94)	3 (2)
C(92)	C(93)	C(94)	C(95)	-2 (2)
C(93)	C(94)	C(95)	C(96)	-2 (2)
C(94)	C(95)	C(96)	C(91)	6 (2)